Boreskov Institute of Catalysis
of the Siberian Branch of Russian Academy of Sciences, Russia

Russian Scientific and Cultural Center in Vienna, Russia

Federal Agency «Rossotrudnichestvo», Russia

Ministry of Education and Science of the Russian Federation

European Federation on Chemical Engineering

Scientific Council on Theoretical Fundamentals of Chemical Technology RAS

Scientific Council on Catalysis RAS

EFCE CONFERENCE
Event 691

XIX International Conference on Chemical Reactors
CHEMREACTOR-19

Vienna, Austria
September 5 – 9, 2010

ABSTRACTS

Novosibirsk, 2010

INTERNATIONAL SCIENTIFIC COMMITTEE

Valentin N. Parmon, **Chairman**	Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
Alexander S. Noskov, **Vice-Chairman**	Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
Dmitry Yu. Murzin, **Vice-Chairman**	Ǻbo Akademi University, Turku, Finland
David Agar	University of Dortmund, Germany
Sergey Alekseenko	Institute of Thermophysics SB RAS, Novosibirsk, Russia
Alex Bell	University of California, Berkeley, CA, USA
Valentin A. Borodulya	A.V. Luikov Heat and Mass Transfer Institute NAS of Belarus, Minsk, Belarus
Jeffery Bricker	UOP LLC, USA
Raghunath Chaudhari	National Chemical Laboratory, Pune, India
Ben A. Christolini	UOP LLC, USA
Jiří Drahoš	Academy of Sciences of the Czech Republic, Prague, Czech Republic
Mike P. Duduković	Washington University, St. Louis, USA
Gerhardt Eigenberger	Stuttgart University, Germany
Pio Forzatti	Technical University of Milan, Italy
Gilbert Froment	Texas A & M University, USA
Jiří Hanika	Institute of Chemical Process Fundamentals, Prague, Czech Republic
Erik Heeres	Rijks Universiteit Groningen, The Netherlands
Valerii A. Kirillov	Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
Nikolay N. Kulov	Kurnakov Institute of General and Inorganic Chemistry RAS, Moscow, Russia
Guy Marin	Ghent University, Belgium
Wolter Prins	Ghent University, Belgium
Valerii Schvets	Mendeleev University of Chemical Technology of Russia, Moscow, Russia
Constantinos G. Vayenas	University of Patras, Greece
Andrey Zagoruiko	Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia

LOCAL SCIENTIFIC COMMITTEE

Andrey N. Zagoruiko, **Chairman**	Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
Victor A. Chumachenko	Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
Sergei I. Reshetnikov	Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
Eugene I. Smirnov	Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
Vadim A. Yakovlev	Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia

ORGANIZING COMMITTEE

Alexander S. Noskov, **Chairman**	Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
Nikolay N. Kulov	Kurnakov Institute of General and Inorganic Chemistry RAS, The Scientific Council on Theoretical Foundations of Chemical Technology RAS, Moscow, Russia
Aigana P. Kagyrmanova	Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
Natalya S. Krylova	Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
Oleg Yu. Ksenofontov	Russian Scientific and Cultural Center, Vienna, Austria
Irina V. Pivovarova	Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
Larisa G. Shubina	Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
Aleksey A. Spiridonov	Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
Tatiana V. Zamulina, **Secretary**	Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
Conference co-organizer, executive representative of the Organizing Committee: **ILIKO TRAVEL company**	

The conference is held under the auspices of the Russian Federation Ministry of Industry and Trade

SILVER SPONSOR

uop

A Honeywell Company

The organizers express their gratitude to

Ministry of Education and Science of the Russian Federation, Moscow, Russia

for the financial support

PLENARY LECTURES

HOW TO DESIGN OPTIMAL CATALYTIC REACTOR? HONORARY PLENARY LECTURE DEDICATED TO PROFESSOR MIKHAIL SLIN'KO

Yurii Sh. Matros

President of Matros Technologies, Inc., St. Louis, MO 63017, USA,
E-mail: yurii@matrostech.com

Professor Mikhail Gavrilovich Slin'ko (1914-2009) was a watershed figure in Russian chemical process engineering. Though he published little and was not very well-known in the West, he is merited among other leading scholars, which established the chemical reaction engineering discipline in its present state.

In the beginning of his carrier just after World War II, M. G. Slin'ko was actively involved in heavy water production through hydrogen isotope separation. This was a secret Soviet weaponry project quickly realized in large scale. As M.G. Slin'ko noted [1], the development was based on calculations and direct scale-up without lengthy stages of pilot testing. At approximately the same time, Prof. G. K. Boreskov and M.G. Slin'ko developed sulfuric acid reactors using advanced technique involving chemical kinetics, transport phenomena, and rigorous mathematical optimization. Apparently, from these early works, M. G. Slin'ko understood power of physic-chemical models for industrial process engineering.

From 1957 to beginning of 70^{s}, M.G. Slin'ko built a team of enthusiastic young scientists and engineers in headed by him Department of Mathematical Modeling in the newly created Institute of Catalysis (Novosibirsk, Russia). His own and his students contributions at this time form a basis for his legacy. M.G. Slin'ko's curiously combined great research and educational activities with vigorous publicizing his mathematical modeling method and results of the Department to Soviet and then Russian chemical engineers.

His commandments for the designers of heterogeneous catalytic processes (see for example [1]) included:

- building a kinetic model as an essential step of reactor design,
- exploring theoretical-optimal conditions and revealing fully maximum potential of the catalyst,

- braking up complex process model to simpler hierarchically connected levels, and studying every level separately,
- emphasizing non-linear phenomena in every level,
- examining process stability and parametric sensitivity,
- applying mathematical methods for reactor process optimization,
- examining reactor aerodynamics.

In this lecture we will assess how the catalytic reactor design methodology has evolved since 1960^s. The content of the presentation will be based on literature review including recent results obtained by our former colleagues in Boreskov Institute of Catalysis.

Most of the examples will be related to gas-phase fixed-bed reactor including tubular reactors for processes of partial oxidation, adiabatic-bed reactors for exothermic reversible processes, and unsteady-state reactors for air pollution control. Intensification of the existing and development of new processes will be discussed.

References

[1]. M.G. Slin’ko, Theor. Found. Chem. Eng., **2007**, Vol. 41, pp. 13-29.

MULTIFUNCTIONAL DEVICES FOR INTENSIFIED CHEMICALS PROCESSING: FROM MICROREACTORS TO SPINNING DISKS

Jaap Schouten, Mart de Croon, Evgeny Rebrov,
John van der Schaaf, Xander Nijhuis

Department of Chemical Engineering and Chemistry,
Eindhoven University of Technology,
P.O. Box 513, 5600 MB Eindhoven, the Netherlands,
J.C.Schouten@tue.nl; www.chem.tue.nl/scr

Abstract

In this presentation a short exploratory expedition will be made along a number of new multifunctional reactor technologies. First, examples will be demonstrated of **microreactors** and microchemical systems that provide intricate geometries with characteristic length scales of 5 - 500 μm for optimum mixing, mass and heat transfer, (catalytic) reaction, and product separation. It will be shown that the benefits of these miniaturized systems can be used to enhance productivity, selectivity, energy efficiency as well as to open up new reaction pathways.

Next, the potential of **solid foam packings** as alternatives to well-known structured catalyst supports will be demonstrated. Solid foam packings are available in a variety of materials and pore sizes. They combine the properties of high surface area and low solid holdup suited for low pressure drop applications in different gas-liquid up/down flow co/countercurrent configurations. High rates of mass transfer are obtained at relatively low energy dissipation.

Finally, the **multiple spinning disks contactor** will be introduced. This technology uses centrifugal accelerations to create thin highly sheared films on rotating surfaces. The fluid dynamics within these films result in significant enhancement in heat and mass transfer rates. The spinning disc reactor operates in continuous mode and noticeably reduces the inventory of hazardous chemicals. Multiple sets of disks can be stacked, leading to a small-scale rotating chemical plant in which characteristic functionalities and unit operations as pumping, compression, mixing, heating, reaction, extraction, evaporation, distillation, or crystallization are fully integrated on interconnected and stacked sets of rotating disks.

These new and challenging reaction and separation technologies provide highly promising perspectives for future small-scale 'green' production plants. Chemicals

processing will be more flexible using these small-sized units and takes place fully automated, just-in-time, close to the raw materials source, and at the location of use.

Characteristic recent publications

Microreactors

M.J.F. Warnier et al., Pressure drop of gas-liquid Taylor flow in round micro capillaries for low to intermediate Reynolds numbers, Microfluidics Nanofluidics, 8(1), 33-45, 2010

S.R.A. de Loos et al., Gas-liquid dynamics at low Reynolds numbers in pillared rectangular micro channels, Microfluidics Nanofluidics, DOI: 10.1007/s10404-009-0525-3

O. Muraza et al., Microwave-assisted hydrothermal synthesis of zeolite beta coatings on ALD-modified borosilicate glass for application in microstructured reactors, Chem. Eng. J., 135S, S117-S120, 2008

E.V. Rebrov et al., Selective hydrogenation of 2-methyl-3-butyne-2-ol in a wall-coated capillary reactor with a $Pd_{25}Zn_{75}/TiO_2$ catalyst, Org. Process Res. Dev., 13(5), 991-998, 2009

E.V. Rebrov et al., Capillary microreactors wall-coated with mesoporous titania thin film catalyst supports, Lab Chip, 9, 503-506, 2009

Solid foam reactors

P.W.A.M. Wenmakers et al., Enhanced liquid-solid mass transfer by carbon nanofibers on solid foam as a catalyst support, Chem. Eng. Sci., 65(-), 247-254, 2010

P.W.A.M. Wenmakers et al., Hairy foam, carbon nanofibers grown on solid foam; a fully accessible, high surface area, graphitic catalyst support, J. Mater. Chem., 18, 2426-2436, 2008

R. Tschentscher et al., Gas-liquid mass transfer in rotating solid foam reactors, Chem. Eng. Sci., 65, 472-479, 2010

C.P. Stemmet et al., In-situ UV-Vis spectroscopy in gas-liquid-solid systems, Chem. Eng. Sci., 65, 267-272, 2010

Rotor-stator spinning disc reactor

M. Meeuwse et al., Gas-liquid mass transfer in a rotor-stator spinning disc reactor, Chem. Eng. Sci., 65, 466-471, 2010

M. Meeuwse et al., Mass transfer in a rotor-stator spinning disc reactor with co-feeding of gas and liquid, Ind. Eng. Chem. Res., **DOI:** 10.1021/ie901301m

DESIGN OF CATALYTIC PROCESSES FOR BIOFUELS PRODUCTION

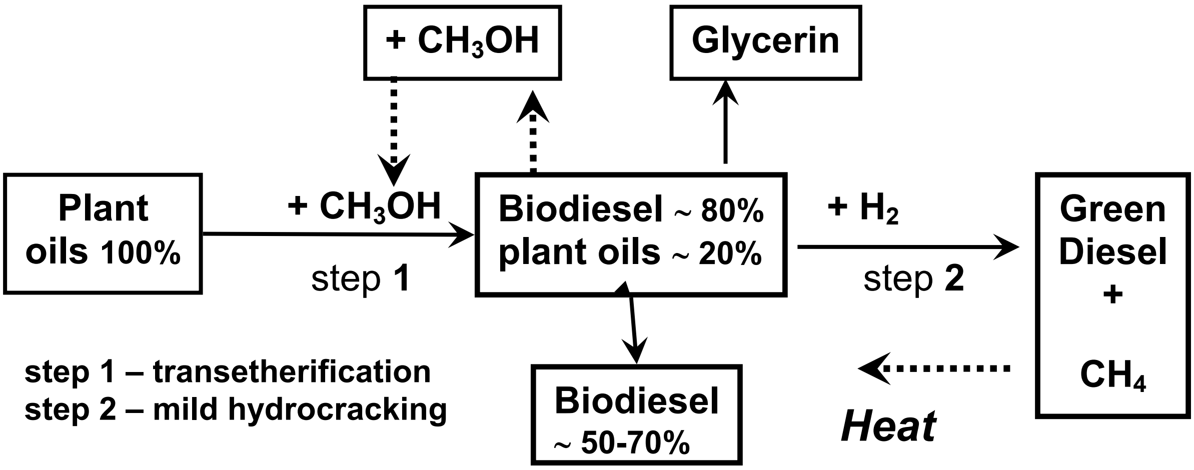
Yakovlev V.A.

Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
E-mail: yakovlev@catalysis.ru

The consumption of petroleum has surged during the 20th century, at least partially because of the rise of the automobile industry. Today, fossil fuels such as coal, oil, and natural gas provide more than three quarters of the world's energy. However at present renewable feedstock attracts attention due to increasing of fossil fuels cost and its graceful irretrievable consumption. At that, now the technologies level of biomass processing into engine fuels is lower than oil-refinery industry. This is a main reason of higher prime cost of bio-fuels production. Bioethanol and biodiesel are produced from food raw materials. Bio-fuels competition with food sector plays negative role for bioenergetics progress. So, for bio-fuels production increasing scientific society has to not only improve present biotechnologies, but develop new biomass processing technologies with widening of renewable feedstock list, including wood and agricultural waste. The new catalytic technologies of biomass processing should play a key role in the bioenergetics evolution.

In Boreskov Institute of Catalysis the intensive investigations are carried out in the field of biodiesel production in the presence of heterogeneous catalysts, high-cetane fuels production from biodiesel and plant oils directly, upgrading of bio-oil – product of wood flash pyrolysis, production of bio-syn-gas and carbonaceous materials.

The specificity of the work is development of new effective catalysts, adjusted to renewable feedstock. The one of developed technology is based on conjugated catalytic processes of transetherification and mild hydrocracking represented on the scheme below:



PL-3

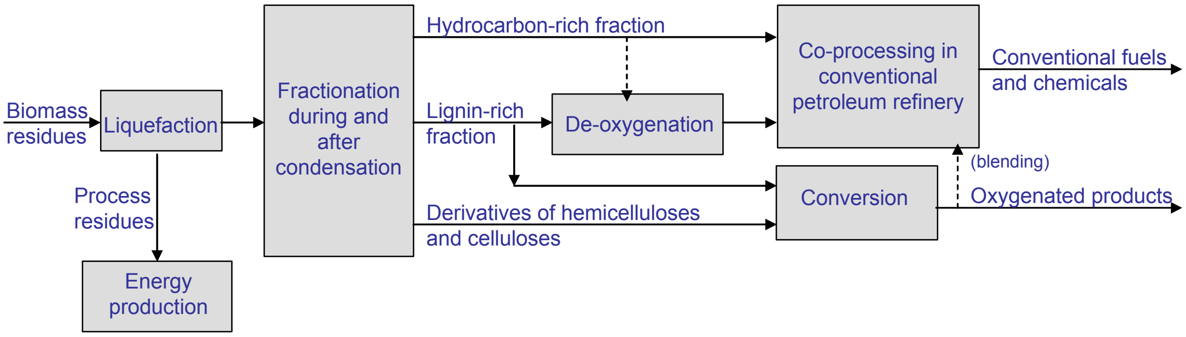
Main features of developed technology are:

- biofuel production of two types: biodiesel and green diesel;
- varying of biodiesel and green diesel yields depending needs;
- optimization of hydrogen consumption;
- energy-supply of both stages via burning of gaseous products, produced on 2nd step.

Catalytic characteristics of the technology include application of heterogeneous basic trasetherification catalysts under 200-220°C and 2.0 MPa and possibility of multiple catalyst regeneration for the first stage. For the second stage these ones comprise using of non-sulfided and non-noble metal catalysts, mild reaction conditions (300-340°C and 2.0 MPa H_2) and possibility of green diesel production with different cetane number via hydroisomerization catalysts application.

The bio-oil, which is a product of flash pyrolysis of grinded wood, is another perspective feedstock for the petrol production. However bio-oil cannot substitute traditional gasoline and diesel in the internal-combustion engines on its own owing to their lower operational properties. The main reason is the high oxygen content in above mentioned bio-fuels. Bioethanol and biodiesel can be used as the additive to gasoline and diesel correspondingly while bio-oil requires catalytic elimination of oxygen from it and simultaneous saturation by hydrogen.

It should be pointed out that one cannot use traditional hydrocracking catalysts for oil-refinery at hydrotreatment of bio-fuels because of low sulfur content in original feedstock. The main reason of these phenomena is reduction of the sulfided Co- or Ni- containing active center to the metal state, followed by coke formation and the catalyst deactivation. When so, sulfur is removed from the catalysts and the target products are contaminated by sulfur. Thus, the objective of the present investigation is to develop non-sulfided catalysts for upgraded bio-fuels production. The obtained upgraded products can be used as additives to fossil crude-oil in the standard oil-refining. On the whole catalytic process development is carried out within FP6 BIOCOUP project with following conception:



Note: hydrocarbon-rich fractions are formed when the biomass feedstock contains a significant amount of extractive substances; e.g the case for forestry residues.

Indeed preparation and testing in target processes such binary catalytic systems has shown that developed mild hydrocracking catalysts permit not only to obtain alkanes C_{11} – C_{17} in one stage with the yield 100% both from biodiesel and from vegetable oils at mild conditions: 260 – 350°C, hydrogen pressure 1,0 – 2,5 MPa, but also to reduce oxygen content in bio-oils in one stage too from 45 wt% until 5 wt% at 320 – 350°C, hydrogen pressure 12–15 MPa.

Acknowledgments

FP6 project № 518312, integration project №2 SB RAS are gratefully acknowledged.

PL-4

HIGH TEMPERATURE PROCESSES OF NANOSTRUCTURAL CARBON MATERIALS PRODUCTION

Likholobov V.

Institute of Hydrocarbons Processing,
Omsk Scientific Center SB RAS, Omsk, Russia

The past decades were marked by impressive achievements in studying the properties of earlier discovered various forms of nanostructural carbon such as fullerenes, nano-onions, nanotubes, nanoglobules, nanofilaments, nanofibrils, graphenes, and others. The obtained results demonstrate that the totality of physical and chemical properties of these materials makes them basic for solving the problems of future nanoindustry. However, technologies underlying the production of such materials in practically significant amounts (kilograms, tonnes) are not far advanced, which is a hindering factor. Irrespective of a recent breakthrough (the tonnage production of C_{60}/C_{70} fullerenes and multiwalled carbon nanotubes), production of nanostructural carbon materials remains quite a topical problem.

Most of the above-listed nanostructural carbon materials are obtained via high temperature decomposition of various hydrocarbons in the gas phase (with solid carbon forming in the gas phase) or in the presence of solids acting as matrix catalysts (with carbon phase growing on a matrix). So, special reactor units are needed for the development of appropriate technological processes.

The lecture considers the production of nanostructural carbon materials from gaseous and liquid hydrocarbon feedstock via the step of carbon nanoglobules generation. Data on the nature of corresponding molecular precursors, factors determining the rate of carbon phase formation, regularities of its growth into nanoglobules and their agglomeration into secondary structures are analyzed. Advanced physical methods, including the high resolution electron microscopy, were used to study the specific structure of primary and secondary particles on micro- and nanoscales.

Operation parameters of the reactor unit producing nanoglobular carbon of a specified structure were determined.

The second part of the lecture deals with the production of special-purpose nanostructural carbon materials from nanoglobular carbon. Such materials are obtained by:

- deposition of lamellar pyrocarbon on nanoglobular carbon followed by nanoglobular carbon burn-out;
- separation of weakly agglomerated high-disperse particles of nanoglobular carbon further exposed to high temperature and pressure;
- exposure of the primary nanoglobules to high-energy ionizing radiation.

The structure of materials forming upon such treatments was investigated; designs of appropriate reactor units were suggested.

In conclusion, the prospects of practical application of the produced materials and some new lines in the synthesis of nanostructural carbon composites are shown.

PL-5

MULTIPHASE CATALYTIC REACTIONS IN REACTORS STRUCTURED AT THE MESO-SCALE

Hugh Stitt[1,*], Dan Enache[1], Steve Pollington[1], Mike Winterbottom[2]

[1]Johnson Matthey plc, Billingham, Cleveland, TS23 1LB, UK
** hugh.stitt@matthey.com*
[2]School of Chem. Eng., University of Birmingham, Edgbaston B15 2TT, UK

Multiphase reactions are very common in the chemical industry. Many industrial reactions, such as hydrogenation, oxidation, carbonylation and hydroformylation take place in two or even three phase conditions[1]. Such processes have to deal with diffusion (or mass transport) limitations. The workhorse of the fine chemicals industry is the stirred batch reactor. This is a versatile reactor and can be used for more than one reaction and more than one product. This multi-reaction and multi-product capability offers huge advantages for batch plant scheduling. But despite advances in the design of the impeller and of the gas sparge pipe, this reactor still presents some disadvantages. They can be inadequately mixed and frequently mixing, mass transfer or heat transfer steps govern the reaction rate. The net result of this is that reaction times tend to increase significantly with increasing scale, leading to reduced operating and thus capital efficiency. Commonly reaction selectivity will also decrease on scaling from batch to plant operation as a direct result of the transport limitations. They are difficult to scale-up as the critical dimensions associated with a multiphase reaction (reactor dimensions, bubbles size, micro-mixing scale and kinetic-related distances) do not scale in proportion; increasing reactor size commonly increases the limitations due to mass and heat transport[2].

There has recently been significant attention to the potential of structured reactors and catalysts to achieve increases in volumetric productivity and controllability[3,4]. This is exemplified by the micro-channel and monolith reactor concepts. In this case, each channel is nominally an independent plug flow reactor and scaling-up simply becomes an issue of increasing the number of channels (scaling-out) as long as flow is equally distributed over all channels[5].

Significant work has been done to demonstrate the process benefits of monolith based catalysts for multi-phase reactions since the pioneering work of Andersson's group at Chalmers University[6]. The preferred operating regime of Taylor flow has been shown to generate high gas-liquid mass transfer coefficients and volumetric rate benefits over conventional reactors (notably stirred tanks) in the order of 10-100 times have been widely reported. The dominant mass transfer mechanism is via the bubble wake (not the thin film between the bubble and catalysed wall as originally believed)[7,8]. The monolith reactor is substantially adiabatic, but recycle process configurations have been proposed to overcome this[9].

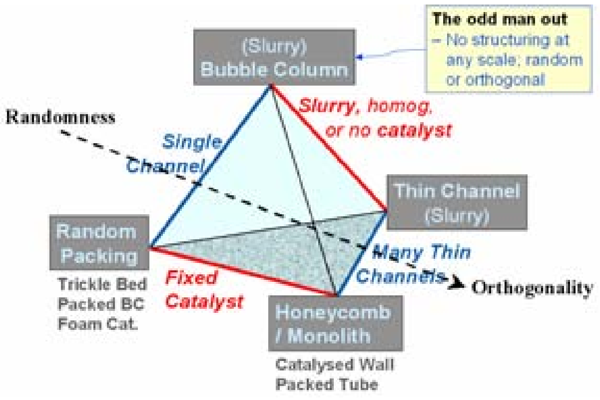
Reactor designs with intensified heat transfer have been available for a number of years, based in many cases on the concepts of compact heat exchangers[10,11]. Use of this type of reactor, generally featuring narrow flow channels and large heat transfer areas, has previously been proposed for single phase liquid reactions[12,13], for liquid–liquid reactions[14], for gas–liquid reactions[15,16] and for heterogeneously catalysed gas liquid reactions with the catalyst either adhered to the channel walls[17], or packed within the flow channels[18].

Trickle bed reactors are used commonly in the refinery and petrochemical industry for hydrogenation-based reactions. This reactor type is continuous in operation and is regarded as a plug flow reactor (Haure et al, 1989, Boelhouwer et al., 2001) and essentially un-structured. Recent work to elicudate the mechanism of flow regime transition (from trickle to pulse) has however highlighted that the hydrodynamics, and thus reaction performance of a trickle bed are dominated by local bed packing structures[19,20]. The trickle bed should therefore be considered as structured, albeit that the structure is random rather than orthogonal

It has of course been proposed variously to “structure” [systematically] trickle beds[21], and indeed the internals of reactive distillation columns (which are after all a multiphase catalytic reaction environment)[22,23,24]

Reticulated foams have received attention in recent years also as substrates for catalysis in multiphase reactions[25]. These may ostensibly be considered as a “negative image” trickle bed, and have the same benefit of high substrate surface areas but the notable benefit of very high packing voidage (>90% rather than ca. 40% in a trickle bed). Studies of these supports appear to indicate that the hydrodynamics here are also dominated by local structures and flow constrictions. The foam based catalyst reactor is therefore also essentially structured, but in a random rather than orthogonal fashion.

From the above it is apparent that only reactors with a void interior space and slurry, homogeneous or no catalyst are truly unstructured: stirred tanks, slurry bubble columns. Considering the classification of reactors according to this logic highlights that the main part of the literature largely misses one important class of reactors: namely a slurry reactor in a structured environment[26]. Studies on this embodiment, either as an adiabatic or as a heat exchange reactor, show that this design also offer significant rate benefits, and changes in selectivity for some chemistries[27,28].



In summary therefore, a significant body of work has been carried out that demonstrates the benefits of reactor structuration at the meso-scale (viz. similar scale to bubbles; 0.5-5 mm say). Despite this, and the supporting evidence in the literature, there has been relatively little commercial implementation in terms of replacing conventional trickle bed and stirred tank reactors. Clearly, the evidence is not as compelling as the proponents (that include the authors of this paper) would like to believe. There are fundamental barriers, such as the relative cost of extrudates for trickle bed packing and monolithic substrates (whether honeycomb or foam). There is, more importantly, a lack of clarity on the key performance parameters for each design option, and relatively few meaningful comparisons of the different design options; for example there are relatively few studies that rigorously compare the trickle bed and monolith reactors[29]. In order to progress implementation of the superior structured reactor and catalyst concepts the research community needs to address specifically where each of these reactor design concepts has unique performance characteristics.

---

[1] Mills & Chaudhari (1997) *Catal. Today* 37, 367–404.

[2] Stitt (2002) *Chem. Eng. J.* 90, 47–60.

[3] Kapteijn, Heiszwolf, Nijhuis & Moulijn, (1999), *Cat-Tech* 3, 24

[4] Cybulski & Moulijn (2006) *Structured Catalysts and Reactors* (2nd Ed.) Pub. Taylor & Francis

[5] Lerou & Ng (1996) *Chem.Eng.Sci.*, *51, 1595*

[6] Irandoust & Andersen (1988): *Chem.Eng.Sci.*, 43, 1983

[7] Bercic and Pintar (1997) *Chem.Eng.Sci,* 52, 3709

[8] Kreutzer, Du, Heiswolf, Kapteijn & Moulijn (2001) *Chem.Eng.Sci*, 56, 6015

[9] Heiszwolf et al. (2005) *App. Cat. A*, 288, 175

[10] Kays & London (1984), Compact Heat Exchangers, 3rd Ed., McGraw-Hill (1st ed. 1955)

[11] Thonon & Tochon (2004) pp. 121–165: Stankiewicz A., Moulijn J.A. (Eds.), Re-Engineering the Chemical Processing Plant, Marcel Dekker.

[12] Edge, Pearce, Phillips, (1997), pp. 175–190 in: Semel J. (Ed.), Proceedings of the Second International Conference on Process Intensification, Antwerp, Pub. BHR Group

[13] Phillips, (1999) pp. 71–87 in: Green A. (Ed.), Proceedings of the third International Conference on Process Intensification, Antwerp, Pub BHR Group.

[14] Green, Johnson, Westall, Bunegar, Symonds (2001), pp. 215 in: Gough M. (Ed.), Better Processes for Better Products, BHR Group, Cranfield, UK,

[15] Wiese, Protzmann, Koch, Roettger, Trocha (2002) *US Patent* 6,492,564

[16] Enache, Thiam, Dumas, Ellwood, Hutchings, Taylor, Hawker & Stitt (2007), *Catal. Today*, 128, 18

[17] Gavriilidis, Angeli, Cao, Yeong & Wan, (2002), *Chem. Eng. Res. Des.* 80(A1) 3

[18] Bavykin, Lapkin, Kolaczkowski & Plucinski (2005) *Appl. Catal. A*: Gen. 288, 175

[19] Lim, Sederman, Gladden & Stitt (2004) *Chem.Eng.Sci*, 59 5403

[20] Anadon, Sederman & Gladden (2006) *A.I.Ch.E. Journal,* 52, 1522 (2006),

[21] Nigam & Larachi (2005) Chem.Eng.Sci 60, 5880-5894

[22] Dautzenberg & Mukherjee (2001) : *Chem.Eng.Sci.*, 56, 251

[23] Calis, … Dautzenberg, van den Bleek (2001) *Chem. Eng. Sci.* 56. 1713

[24] Urseanu, Ellenberger & Krishna (2001), *Cat.Today*, 69, 105

[25] Stemmet, van der Schaaf, Kuster & Schouten (2006), *Trans.I.Chem.E*, 84(A12), 1134

[26] Stitt & Winterbottom (2006) *Patent Application*, WO2006 104401 A1

[27] Enache, Hutchings, Taylor, Natividad, Raymahassay, Winterbottom & Stitt (2005) *Ind.Eng.Chem.Res.* 44, 6295

[28] Pollington, Enache, Landon, Meenakshisundaram, Dimitratos, Wagland, Hutchings & Stitt (2009) *Cat.Today* 145, 169–175

[29] (a) Edvinsson & Cybulski (1994) Chem.Eng.Sci 49 5653-5666;
(b) Edvinsson & Cybulski (1995) *Catalysis Today* 24, 173-179
(c) Nijhuis, Dautzenberg & Moulijn (2003) *Chem Eng.Sci*, 58, 1113-1124
(d) Enache, Landon, Lok, Pollington & Stitt (2005) *I.E.C.Research*, 44, 9431
(e) Fishwick, Natividad, Kulkarni, McGuire, Wood, Winterbottom & Stitt (2007) *Cat.Today* 128, 108–114

MEMBRANE REACTORS: STATE OF THE ART AND PERSPECTIVES IN BIOTECHNOLOGY AND CHEMICAL PRODUCTION

Lidietta Giorno

Institute on Membrane Technology, ITM-CNR, 87036 Rende CS, Italy
Tel. +39 0984 492050, Fax: +39 0984 402103, l.giorno@itm.cnr.it,
Lidietta.Giorno@cnr.it www.itm.cnr.it, www.emsoc.eu

Membrane processes are state of the art technologies in various industrial sectors, including gas separation, waste water treatment, food processing and medical applications. More recent processes, such as membrane reactors, are developing very fast. The optimal design of chemical transformation processes with control of reagent supply and/or product removal through catalytic membranes and membrane reactors is one of the most attractive solution in process intensification.

The catalytic action of biocatalysts is extremely efficient, selective and highly stereo-specific when compared to conventional chemical catalysts. Membrane bioreactors are particularly attractive in terms of eco-compatibility, because they do not require additives, are able to operate at moderate temperature and pressure, reduce the formation of by-products while permitting the production of high valuable co-products. This may allow facing challenges in developing new production lines moving towards zero discharge.

The major market for membrane bioreactors is represented by wastewater treatment with the use of submerged modules configuration. These are considered among the best available technologies by European Directives on Environment. Biochemical membrane reactors are also applied in food, red and white biotechnology. In these cases, the external loop configuration is used. Industrial applications include production of amino acids, antibiotics, anti-inflammatories, anticancer drugs, vitamins, optically pure enantiomers. Applications in green and blue biotechnology for integrative energy from renewable resources (such as algae and micro algae) will attract much attention. The development of submerged biocatalytic membrane reactors for production of fine chemicals is also in progress.

The main technological difficulties in using biochemical membrane reactors for production on an industrial level are related with rate-limiting aspects and reproducibility on large scale, together with the life-time of the enzyme, the availability of pure catalysts at an acceptable cost, the necessity for biocatalysts to operate at low substrate concentration and without microbial contamination.

Many studies are oriented to the investigation of operating conditions and optimization of the various properties of membrane bioreactors. However efforts towards the development of a predictive approach, able to overcome the trial and error one, is necessary to significantly advance the field. The development of membranes specifically designed to answer bioreactor needs is necessary as well.

The converging of technologies such as genetic engineering, bioprocess design, molecular modelling, biochemical engineering, electronic engineering will promote innovative solutions to face the need of precise, selective, clean, safe, low energy consumption and eco-friendly processes, such as biochemical membrane reactors.

The development of catalytic membrane reactors for high temperature applications became realistic more recently, with the development of high temperature resistant membranes. However, besides fuel cells, so far, no high temperature membrane reactor in operation on a productive scale is reported in the open literature.

Typical examples of chemical reactions with inorganic membrane reactors include dehydrogenation, where hydrogen is removed, oxidation and hydrogenation, where oxygen and hydrogen are added, partial oxidation, isomerization and esterification. Membrane reactors can be particularly advantageous for sequential endothermic and exothermic reactions, by using the product extraction to promote heat transfer, with the net result of smaller reactors, lower capital costs, and often fewer side-reactions.

In general, nowadays the attention towards membrane reactors is increasing significantly. Drivers of this interest include the need of technologies enabling sustainable production, directives and regulations about the use of eco-friendly technologies, consumer demand of high quality and safe products, public concern about environment, stakeholders confidence in and acceptance of advanced technologies.

Current initiatives recognize that a sustainable solution to the increasing demand of goods and energy is in the rational integration and implementation of new technologies able to achieve concrete benefits of manufacturing and processing, substantially increasing process precision, reducing equipment size, saving energy, reducing costs, minimizing environmental impact. Membrane reactors best suit in this context as their basic aspects well satisfy the requirements of process intensification for a sustainable industrial production. In fact, they are precise and flexible processing techniques, able to maximize phase contact, integrate conversion and separation processes, with improved efficiency and with significant lower energy requirement compared to conventional techniques.

KEY-NOTE PRESENTATIONS

KN-1

OXIDATIVE COUPLING OF METHANE. THIRTY YEARS OF STUDIES: FROM PHENOMENOLOGICAL TO NON-CONTRADICTORY KINETIC DESCRIPTION

Sinev M.Yu.[1], **Tulenin Yu.P.**[1], **Fattakhova Z.T.**[1],
Lomonosov V.I.[2], **Gordienko Yu.A.**[2]

[1]Semenov Institute of Chemical Physics, R.A.S., Moscow, Russia,
E-mail: sinev@chph.ras.ru
[2]ZAO "SCHAG" Company, Moscow, Russia

Oxidative coupling of methane (OCM) to higher hydrocarbons, that was discovered in early 1980's [1-3], is one of attractive methods of natural gas transformation to value-added products. During the passed three decades the main features of OCM mechanism have been elucidated and for a number of systems (mainly - oxides, simple and complex) a high efficiency as OCM catalysts was demonstrated. It was shown that because of the mechanistic and kinetic reasons, the process under discussion can efficiently proceed only at high temperatures (above 1000 K), and only a limited per-pass yield (20-25%) of target products (C_2-hydrocarbons, first of all, ethylene) can be achieved due to their higher reactivity as compared to methane. These two factors are among those hampering the practical implementation of the OCM process.

Also, the development of adequate kinetic model is an indispensable condition for the transfer from a phenomenological description to the process engineering and scaling-up. However, the compilation of really-working kinetic OCM model meets serious obstacles due to a complex free-radical heterogeneous-homogeneous nature of the process under consideration. On the one hand, multi-step kinetic schemes similar to those used to describe homogeneous gas reactions reflex the intrinsic features of the process and can be used for mechanistic studies. Unfortunately, the uncertainty in kinetic parameters does not allow one to utilize such schemes for a quantitative description of the process that is required for its practical implementation.

An alternative approach that describes the formation of the final products (mainly C_2-hydrocarbons and carbon oxides) by the limited number of stoichiometric reactions and corresponding kinetic equations (based on the mass-action and Arrhenius laws) is able to assure any prescribed accuracy, but only within relatively narrow limits of parameters achieved during the model experiments. Such kinetic description, that can be characterized as empirical, may suffer from a poor validity and low predictive power beyond the above mentioned limits.

In this work an approach to non-contradictory description of the OCM kinetics is formulated and discussed. It consists in the modeling of the OCM kinetics based on the independent mechanistic data that demonstrate the redox nature of the target process. The latter presumes that the main reaction pathways, such as

$$CH_4\ (+\ O_2) \rightarrow CH_3^{\bullet}\ (\rightarrow C_2H_6)$$

and

$$C_2H_6\ (+\ O_2) \rightarrow C_2H_4$$

can be described in the framework of Mars-van Krevelen type kinetic schemes. The second main assumption consists in the assignment of "blocks" of elementary free-radical reactions (with corresponding rate constants) to the key parts of the overall catalytic process (such as reduction and re-oxidation of active sites, formation of by-products, etc.). This allows one to assign a certain physical meaning to apparent parameters that enter into the kinetic equations and to pre-evaluate the reasonable limits of their values.

This approach was tested on typical OCM catalysts (PbO/Al_2O_3, $NaWMn/SiO_2$, Ln-Mg-oxides) and demonstrated its ability to describe not only "smooth" kinetic curves and general trends (reaction rate vs. temperature, GHSV, reactant partial pressures; product selectivities vs. conversion, etc.), but also some non-trivial effects (such as competitive/stimulating reciprocal influence of hydrocarbons, non-linear selectivity trends, complex effects of additives, such as peroxides, etc.).

It was concluded that although the detailed multi-step and the empirical descriptions of the OCM kinetics are conceptually different, they both reflect some basic features of the process under consideration and are complementary. Being used simultaneously, they can substantially improve the accuracy, the validity and the predictive power of the kinetic description of the process under consideration.

References

[1]. M.L. Mitchell and R.H. Waghorne. US Patent No. 4205194 (**1980**).
[2]. T. Fang and C. Yeh. J. Catal., **1981**, v.69, p.227.
[3]. G.E. Keller and M.M. Bhasin. J. Catal., **1982**, v.73, p.9.

KN-2

REVERSED-FLOW REACTORS: POTENTIAL AND REALIZED

Bunimovich G.A. and **Matros Yu.Sh.**

Matros Technologies, Inc., St. Louis, MO 63017, USA,
E-mail: grigorii@matrostech.com

The reversed-flow reactor (RFR) combines chemical processes with regenerative heat exchange or adsorption in fixed bed units. The system realizes bell-shaped concave or convex profiles of temperature or concentration of adsorbed compounds along the bed length. For gas-phase exothermic processes the heat can be effectively trapped in the center of the bed at low temperature of inlet and outlet gas. The efficiency of heat recuperation can reach 95%-97%, which is important for such processes as thermal or catalytic oxidation of volatile organic compounds in diluted air or gases.

This paper is suggested for a key-note presentation. We will review the history, current status and challenges in reversed-flow reactor technology. The presentation will be focused more on commercially realized processes.

The original development of a heat-trapping RFR for exothermic reversible reaction such as oxidation of SO_2 to SO_3 [1-3] was followed by more complex ideas including asymmetric reactors combining exothermic and endothermic processes [4-7], adsorptive reactors [8-9] and reactors with retained carried-over catalyst [10]. We will discuss the RFR applications tested in pilot scale: automotive converters [11], asymmetric fuel reformers [6-7], and zone reactor for bromine-mediated functialization of methane [9].

The following part of the presentation will briefly review the reactor fundamentals. Even a simple one-dimensional model demonstrated rather complex behavior including multiplicity of “periodic” steady states as well as quasi-periodic and chaotic operations [12-15]. The issues of stability and parametric sensitivity are important for large-scale RFRs where the beds can have spatial non-uniformities, and problems with catalyst overheating and process stabilization and control can arise. Another important challenge relates to temperature profile optimization for achieving high reactant conversion. The presentation will discuss solutions adopted in some applications.

Commercial reversed-flow reactors were developed for oxidation of SO_2 in sulfuric acid production, complete oxidation of volatile organic compounds (VOC), selective catalytic reduction of NO_x, abatement of low concentrated methane, and decomposition of N_2O.

Substantial fraction of the presentation will be devoted to VOC control, where the RFRs were realized in thousand units. The authors will share their experience with various VOC applications. We will evaluate the process energy efficiency and economics, requirements to VOC oxidation catalysts, catalyst deactivation and regeneration, and transitions from thermal to catalytic oxidizers [16].

References

[1]. Yu.Sh. Matros, **1989**. Catalytic processes under unsteady-state conditions. Studies of Surface Science and Catalysis, 43, Elsevier.

[2]. G. K. Boreskov, Yu. Sh. Matros, O. V. Kiselev, and G. A. Bunimovich, Doklady Akademii Nauk SSSR, [Doklady Chemical Technology], **1977**, 237, 160-163.

[3]. G.K. Boreskov, Yu. Sh. Matros, G. A. Bunimovich, and A.A. Ivanov, Kinetic. Catal.*,* **1984***, Vol. 23,* pp. 335-342.

[4]. M. S. Kulkarni, and M. P. Dudukovic, AIChE Journal, **1996**, Vol 42, pp. 2897–2910.

[5]. G. Kolios, and G. Eigenberger, Chem Eng Sci., **1999**, Vol. 54, pp. 2637-2646; B. Glockler, G. Kolios, and G. Eigenberger, **2003**, Chem Eng Sci, Vol. 58, pp. 593–601.

[6]. F. Hershkowitz, H. W. Deckmana, J. W. Frederick, J. W. Fultonb, and R. F. Sochaa, Energy Procedia, **2009**, Vol. 1. pp. 683-688.

[7]. B. Glöckler, H. Dieter, G. Eigenberger, and U. Nieken, Chem Ebg Sci., **2007**, 62, 5638 – 5643.

[8]. D. W. Agar, Che Eng Sci., **1999,** Vol. 54, pp. 1299-1305.

[9]. A. Breed, M. F. Doherty, S. Gadewar, P. Grosso, I. M. Lorkovic, E. W. McFarland, and M. J. Weiss, Catalysis Today, **2005,** Vol. 106, pp. 301-304.

[10].K. G. W. Hung**,** D. Papadias, P Bjornbom, M. Anderlund, and B. Akerman, AIChE Journal, **2003**, Vo. 49, pp. 151-167.

[11].Yu. Sh. Matros, G. A. Bunimovich, V. O. Strots and E. A. Mirosh, **1999,** Chem Eng Sci., Vol. 54, no. 13-14, pp. 2889-2898.

[12].G.K. Boreskov, G. A. Bunimovich, Yu. Sh. Matros, O. V. Kiselev, and I.A. Zolotarski, Doklady Akademii Nauk [Doklady Chemical Technology], **1983**, vol. 268*,* p. 646.

[13].J. Řeháček, M. Kubíček, and M. Marek, Chem Eng Sci., **1992**, Vol. 47, p. 2897-2902.

[14].A.G. Salinger, and G. Eigenberger, Chem Eng Sci., **1996**, Vol. 51, pp. 4903-4915 and pp. 4915-4922.

[15].J. Khinast, Y. O. Jeong, and D. Luss, AIChE Journal, **1999**, Vol. 45*,* pp. 299-309.

[16].G. A. Bunimovich and Yu. Sh. Matros, Chemical Engineering, **2010**, No. 3, pp. 2-7.

KN-3

THE MECHANISM OF NANOCLUSTER COMBUSTION OF NON-STANDARD FUEL AND APPROPRIATE FURNACE UNIT

Alekseenko S.V.[1,2], Paschenko S.E.[2], and Salomatov V.V.[1,2]

[1]*Institute of Thermophysics SB RAS, Novosibirsk, Russia*
E-mail: vvs@itp.nsc.ru
[2]*Novosibirsk State University, Novosibirsk, Russia*
E-mail: Pashenko-ecolog@yandex.ru

The non-renewable hydrocarbon energy-carriers are the basis of the world fuel resource. However, the problem of fuel supply is relatively urgent because of forthcoming exhaust of convenient and available gaseous and liquid energy-carriers of a high quality. Under these conditions numerous available off-grade fuels and combustible man-made wastes are still out of use. These large-tonnage off-grade fuels and wastes include: water-coal sludge of coal-concentrating and coal-mining plants; waste motor oils, lubricants, contaminated mazuts, non-utilized products of oil processing (oil sludge, tars), and other combustible materials. The main reason for insufficiently useful utilization of these waste combustibles is a lack of modern high-efficient furnace units for such fuels.

We have suggested a new method for combustion of hydrocarbon-bearing off-grade liquid fuels [1]. The feature of this method is separate supply of two flows into the combustion chamber: fuel+air and superheated steam. The initial flame is generated at off-grade fuel combustion under the conditions of partial or total blocking of air (oxidizer) supply. As a result, the aerosol soot flame with the given particle parameters is formed at the initial stage in the combustion chamber. Then, the secondary flame is formed due to a pulse of superheated steam. In our opinion, in this secondary flame catalytic decomposition of steam molecules occurs on clusters of soot nanoparticles. This leads to conditions required for efficient ignition of “heavy” fuels and their stable combustion.

The series of standard evaluation burners with the power of 5 – 20 kW was made on the basis of this physical-chemical mechanism. The experimental 20-kW burner is shown in Fig.1. Stainless steel burner shell 1 is made of the welded co-axial rings, where distilled water is fed in-between them through hole 2. The evaporating and steam-superheating surfaces of the mini steam generator are imbedded in the same place. Liquid fuel from the fuel tank is fed into a metal tray by gravity through fitting 4, connected from beneath to the burner shell. Superheated steam produced in the mini steam generator passes through steam pipeline 8 to nozzle block 3.

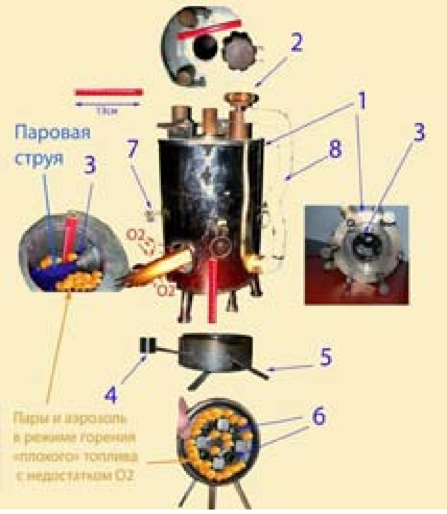


Fig. 1. Experimental burner of 20 kW.

1 – doubled shell with water, 2 – hole for water supply, 3 – nozzle with superheated steam, 4 – inlet valve of straw oil, 5 – drain of excess fuel, 6 – holes for bottom leak-in of air, 7 – doors for regulation of steam pressure, 8 – pipeline for superheated steam.

The following results were obtained by means of the modern sensors and unique experimental equipment:1) different types of soot particles were distinguished on the basis of electron microscopy; according to the analysis, the particles of the fractal type, consisting of initial particles of the nanometric range, will be always found in the bulk even in the presence of “large particles” (parts of microns); 2) according to the working hypothesis, namely the nanosoot particles can be the centers of increased catalytic activity of steam decomposition with production of chemically active OH radical. The evidence of its presence is glow of OH radical in the close UV range at application of the interference filters; 3) the high-speed video recording with high magnification of the mixing zone allowed registration the pulsation pattern of ignition and final burning of aerosols at the boundary of a steam jet and cloud of soot particles; 4) a change in the spectrum of sound pulsations of the flame allowed distinguishing of the basic harmonics at frequencies of 800-1000 Hz, corresponding to the optimal combustion conditions.

The tests of evaluation burner have shown the following advantages. The level of CO emissions is 200 times lower, and the level of NO emissions it is 18 times lower In comparison with Weishaupt burner (Germany). The burner is totally self-regulating (it does not require additional sources of energy, such as electric, pneumatic, etc.) and has no movable and abradable components. No auxiliary equipment (pump, compressor, automatic devices, etc.) is required. The device operates reliably under unfavorable weather conditions (snow, rain, strong wind, etc.) and does not need permanent monitoring. It is multifunctional, fire-safe, reliable and applicable for a wide range of substandard fuels. The cost of device is lower as compared with conventional prototypes.

References

[1]. Patent of RF No. 2219435 “The method of soot-free combustion of fuel”, Vigriyanov M.S., Salomatov V.V., Alekseenko S.V. of 20.12.2003, Bulletin of inventions No. 35.

KN-4

DEVELOPMENT OF AN INTERNAL REFORMING METHANOL FUEL CELL: CONCEPT, CHALLENGES AND OPPORTUNITIES

Avgouropoulos G.[1], **Ioannides T.**[1], **Kallitsis J.K.**[1,2,3], **Neophytides S.**[1,3]

[1]*FORTH/ICE-HT, Stadiou str., Platani P.O. Box 1414, Patras GR-26504 (Greece),*
E-mail: geoavg@iceht.forth.gr
[2]*Department of Chemistry, University of Patras, GR-26504 Patras (Greece)*
[3]*Advent Technologies SA, Patras Science Park, GR-26504 (Greece)*

Introduction

Though H_2 is being considered as the optimum fuel for fuel cells, its low volume energy density renders its use difficult in mobile or portable applications. The direct and efficient processing of methanol has been considered as a potential alternative [1]. Recent advances in the development of polymer electrolyte membranes (e.g. PBI, Advent TPS) [1] and electrocatalysts, allow the operation of PEMFCs at ~180°C with a reformate gas containing up to 2% CO.

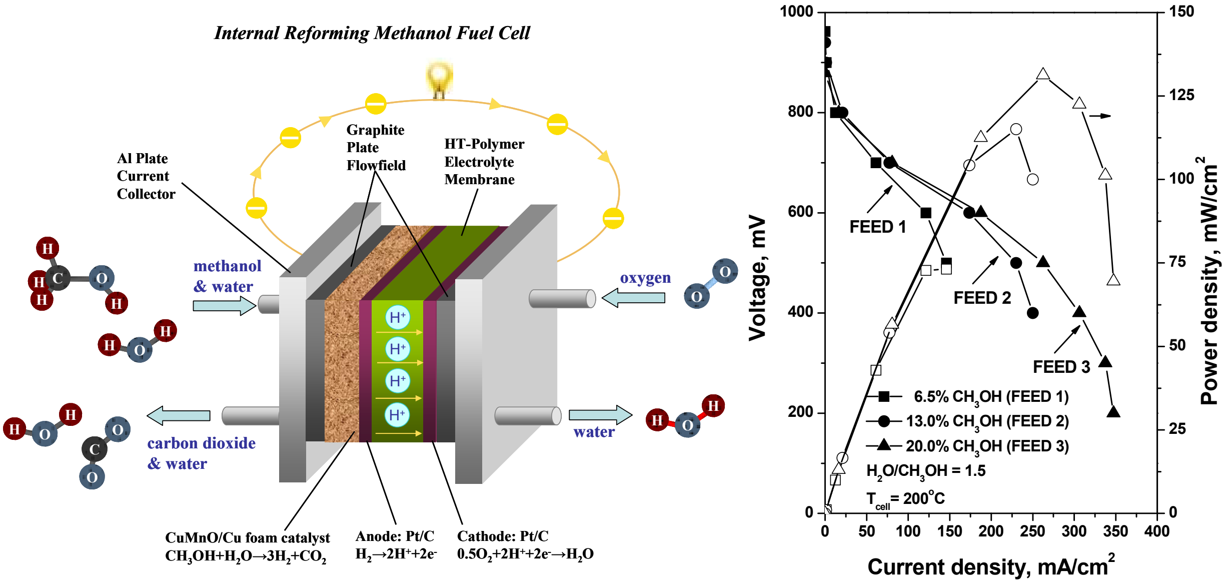


Fig. 1: Integrated reformed methanol HT-PEMFC configuration and polarization curves.

Concept of Internal Reforming Methanol HT-PEM Fuel Cell (IRMFC)

The complexity of the balance of plant of a fuel cell-fuel processor unit challenges the design and development of compact and user friendly fuel cell power systems. In response to this challenge, we propose the compact system [1,2] depicted in Fig. 1. The main concept is the incorporation of a methanol reforming catalyst into the anodic compartment of the fuel cell, so that methanol reforming takes place inside the fuel cell stack (Internal Reforming). The proposed fuel cell comprises: (i) A high temperature membrane electrode assembly (HT-MEA), being able to operate at

~200°C. This is based on the H_3PO_4-imbibed HT-MEAs developed by ADVENT technologies [1], which are not permeable to methanol and have proven long operation at 200°C with minimal H_3PO_4 loss. (ii) A reforming catalyst (e.g. Cu-Mn-O) [1], which is functional at the operating temperature of the fuel cell (i.e. 200°C) producing a CO-free reformate gas. The catalyst is deposited on the surface of metallic copper foam. Alternatively, it can be either present together with the Pt-based anode electrocatalyst or deposited on the gas diffusion layer. Such configurations eliminate the need for separate fuel-processing systems.

Methanol is being reformed inside the anode compartment of the fuel cell at 200°C producing H_2, which is readily oxidized at the anode to produce electricity. The "waste" heat of the cell is utilized in-situ to drive the endothermic methanol reforming reaction, thus eliminating the need for heat exchangers and other voluminous supporting equipment. The IRMFC operated efficiently for more than 72 h at 200°C with a current density of 263 mA cm^{-2} at 500 mV, when 20% CH_3OH/30% H_2O/He (anode feed) and pure O_2 (cathode feed) were supplied (Fig. 1). Its open circuit voltage was 990 mV. It was interestingly observed that due to H_2 utilization/depletion at the anode the reforming reaction rate was enhanced even up to 20%. It is estimated that a sixfold increase in the system's volume power density can be achieved as compared to the conventional combination of a reformer and a PEMFC.

Challenges and Opportunities

The development of an IRMFC poses an ambitious technological and research challenge which requires the effective combination of various technological approaches as regards materials development, chemical reaction engineering and stack design. It aims at opening new scientific and engineering prospects, which may allow easier penetration of the fuel cell system in the energy market. The core of innovation in the IRMFC is the incorporation of an alcohol reforming catalyst into/adjacent to the anode (bi-functional anode) of the HT-PEM fuel cell. In order to obtain an economically viable solution towards the H_2 economy, low-cost materials (electrolytes, catalysts and bipolar plates) and production techniques, with easy maintenance and high durability and stability should be employed.

References

[1]. G. Avgouropoulos, J. Papavasiliou, M. Daletou, T. Ioannides, J. Kallitsis, S. Neophytides, *Appl. Catal. B: Environ.* 90 (2009) 628-632.

[2]. Avgouropoulos, G., Papavasiliou, J., Daletou, M., Geormezi, M., Triantafyllopoulos, N., Ioannides, T., Kallitsis, J., and Neophytides, S., United States Patent Application No: 61/095,779.

KN-5

BIOMASS TO OLEFINS: CRACKING OF RENEWABLE NAPHTHA

Van Geem K.M.[1], **Abhari R.**[2], **Pyl S.**[1], **Reyniers M.**[1], **Marin G.B.**[1]

[1]*Laboratorium voor Chemische Technologie, Universiteit Gent, Technologiepark 918,*
9052 Zwijnaarde, Belgium, e-mail: kevin.vangeem@ugent.be
[2]*Syntroleum®, 5416 S. Yale Ave. Suite 400, Tulsa, OK 74135, USA*

The recent high oil prices and increasing concern about global warming have focused research attention to alternative routes and feedstocks for the production of light olefins. A promising route for the production of olefins from wastes and renewable fractions is the combination of the Bio-Synfining™ process with a traditional steam cracker. Syntroleum's patent-pending[1;2] Bio-Synfining™ process catalytically converts the triglycerides and/or fatty acids from fats, algae and vegetable oils to a high quality synthetic paraffinic kerosene (SPK) or diesel and a renewable naphtha in three steps. First, the raw feedstocks are treated to remove catalyst poisons and water. In the second step, the fatty acid chains are deoxygenated and transformed into mainly paraffins in a hydrotreater. For most bio-oils, fats, and greases, the hydrotreater liquid product consists mainly of C15-C18 paraffins. In the third step of the process, these long straight-chain paraffins are hydrocracked into shorter branched paraffins. The hydrocracked products fall mainly in the kerosene and naphtha boiling range.

The current contribution will discuss on the one hand details about the Bio-Synfining™ Process. Bio-Synfining™ converts low value bio oils to paraffinic diesel or jet fuel, LPG, and naphtha. All the steps of the Bio-Synfining™ process have been demonstrated at the pilot scale and will be discussed. Commercially available hydrotreating catalysts were available in the two stage hydrodeoxygenation (HDO) reactor system used in the pilot tests. With the acid-wash pretreatment step, the HDO catalyst activity remained stable during the four-month pilot plant tests. The naphtha fraction from the hydrocracked HDO paraffins was in the 0.69-0.71 specific gravity range regardless of whether diesel or jet fuel was produced.

On the other hand the contribution will discuss the results of an extensive steam cracking pilot plant campaign performed with renewable naphtha from the Bio-Synfining™ process. This study was performed on the pilot plant of the Laboratorium voor Chemische Technologie[3;4] (LCT) in Ghent university and involved the detailed characterization of the naphtha using GC×GC TOF-MS and GC×GC FID important for addressing the quality of the produced naphtha (detailed PIONA, sulfur, nitrogen and oxygenates content, etc.). Cracking of the renewable naphtha leads to high light olefin yields and low amounts of aromatics. For a residence time of 0.4 s, a Coil Outlet Pressure (COP) of 1.7 bar, a dilution of 0.45 kg steam per kg hydrocarbons and Coil Outlet Temperature (COT) of 850°C, the renewable naphtha gives an ethylene yield of 31 wt% and a propylene yield of 17.5 wt%. The absence of a significant naphthenic and aromatic fraction in the feed results in low C5+ yields, low amounts of pyrolysis gasoline and an almost non-existing amount of pyrolysis fuel oil. The influence of the process conditions on the product yields is as expected.[5] At higher severities more methane, ethylene, 1,3-cyclopentadiene, benzene and toluene are formed. The propylene yield is highest at a COT of 820°C. Higher dilutions result in higher light olefin yields and lower amounts of C5+ products for identical process-gas-temperature profiles. Comparison with results obtained of several oil derived naphthas shows that the renewable naphtha can be considered as a very attractive feedstock for a steam cracker. The latter is confirmed by coking runs [COT = 850°C; δ = 0.45 kg/kg; COP = 1.7 bar] with and without DMDS addition and comparison with coking data of reference feeds. The renewable naphtha has a low coking tendency, and long run lengths can be expected. The results obtained in this study are scaled-up to industrial furnaces using COILSIM1D[6;7], resulting in product yields and run lengths for a typical range of industrial operating conditions.

References

[1]. Abhari, R., Tomlinson, H. L., Havlik, P. Z., and Jannasch, N. L. USA **2008**.

[2]. Abhari, R. and Havlik, P. Z. USA Patent 2009/0163744 **2009**.

[3]. Dhuyvetter, I.; Reyniers, M. F.; Froment, G. F.; Marin, G. B.; Viennet, D. Industrial & Engineering Chemistry Research **2001**, 40, 4353-4362.

[4]. Wang, J. D.; Reyniers, M. F.; Van Geem, K. M.; Marin, G. B. Industrial & Engineering Chemistry Research **2008**, 47.

[5]. Van Geem, K. M.; Reyniers, M. F.; Marin, G. B. Oil&Gas Science and technology - Revue de l'institut français du pétrole **2008**, 63, 79-94.

[6]. Van Geem, K. M.; Zhou, Z.; Reyniers, M. F.; Marin, G. B. Effect of Operating Conditions and Feedstock Composition on Run lengths of Steam Cracking Coils. AIChE Spring Meeting: Ethylene producers conference. **2009**. 30-4-2009.

[7]. Van Geem, K. M.; Reyniers, M. F.; Marin, G. B. Taking optimal advantage of feedstock flexibility with COILSIM1D. AIChE Spring Meeting: Ethylene producers conference. **2008**. 15-4-2008.

Acknowledgements

KVG holds a Postdoctoral Fellowship of the Fund for Scientific Research Flanders and BOF tenure track position at Ghent University. SP acknowledges the financial support provided by the Methusalem project Multi-scale Modeling and design of chemical Reactions and Reactors awarded to Prof. Guy B. Marin.

KN-6

REACTOR MODELLING FOR THIRD GENERATION BIOFUELS PRODUCTION

González A.[1], Kafarov V.[1], Guzman A.[2]

[1]Industrial University of Santander, Chemical Engineering Department,
Calle 27 con Carrera 9 Bucaramanga, Colombia;
[2]Colombian Petroleum Institute ICP-ECOPETROL
Km. 7 via Piedecuesta, Piedecuesta, Colombia;
Tel +57 7 6344000 ext. 2603, e-mail: cisyc@uis.edu.co

Third generation biofuels also called oilgae are based in emerging technologies that ensures high fuel production per area unit and lower production costs. Microalgae oil appears as a promising biodiesel source due to their oil content is many times bigger than oil content of other vegetal sources currently used. Organosolv pretreatment of biomass, extraction and transesterification of microalgal oil are important steps in the biodiesel production chain, organosolv pretreatment helps to separate the strong bonds of the solid matrix making easier the release of the algal compounds and liberating cellulose for another uses, extraction method gives in a great way a measurement of the total process efficiency, and transesterification step contributes appreciably to the quality of the biodiesel and co products obtained due to the operating conditions of the reaction.

This work shows the design of a multifunctional reactor for simultaneous microalgal biomass organosolv pretreatment, microalgal oil extraction and transesterification of fatty acid ethyl esters followed by a separation of the products and ethanol production from the cellulosic biomass pretreated, this design is proposed in order to contribute to the process integration; the multifunctional reactor takes advantage of the use of ethanol for organosolv pretreatment for break down the lignin-carbohydrate complex present in the microalgae biomass, and the need of the presence of the same alcohol as a reagent for the transesterification process.

Into the reactor, the algal biomass is mixed with ethanol and a potassium hydroxide solution, the chemical process begins with the internal lignin, lignin-hemicellulose and glycosidic bonds are hydrolysis, followed by the degradation of the monosacharides, and the solvation and solubilization of the lignin residues, with this process, the oil present in the microalgal biomass is released, such as the another microalgae components trapped in the cell wall like proteins, carotenoids and polymers. after that, the operating conditions are changed in order to start the transesterification reaction with ethanol and the basic catalyst, obtaining biodiesel and glycerol as products, all the products obtained are separated and the organosolv pretreated biomass is submitted to a simultaneous saccharification and fermentation (SSF) process for bioethanol production, this bioethanol is returned to the process as a reagent for the transesterification and organosolv pretreatment.

Optimization of microalgal biodiesel and bioethanol yield, and reaction parameters for obtaining biodiesel with high quality were performed using the software FEMLAB®, the management of the selectivity to the desired products thought management of the reactor operating conditions and parameters is also showed, according with the biorefinery concept. Operating conditions were fixed looking towards a possible application in a pilot plant scale.

Is shown that the multifunctional reactor designed works as a simultaneous third generation biofuels producer and a one step organosolv pretreatment, oil extractor and biodiesel transesterification processes reactor.

The authors thanks to the Iberoamerican Science & Technology Development Programme CYTED, the international project 306RTO279 “New technologies for biofuels production” UNESCO code 330303,332205,530603,330399, the Colombian Agriculture & Rural Development Ministry, and the Colombian Petroleum Institute ICP-ECOPETROL for supporting this work.

KN-7

H_2 PRODUCTION BY METHANE DECOMPOSITION OVER Ni AND Co THIN LAYER CATALYSTS: ROLE OF MSI IN DRIVING THE COKE FORMATION MECHANISM

Frusteri F.[1], Italiano G.[2] and Parmaliana A.[2†]

[1]CNR-ITAE "Nicola Giordano", Via S. Lucia sopra Contesse,
5 – 98126 – Messina, Italy
[2]Messina University, Dept. of Industrial Chemistry,
Salita Sperone 31 – 98166 – Messina, Italy

A reversible cyclic stepwise process based on catalytic decomposition of natural gas (CDNG) and carbon removal could represent a suitable technology for small scale hydrogen production for fuel cell application. The catalytic decomposition of natural gas (CDNG) into hydrogen and carbon is attracting much research interest since it appears to be a direct, mildly endothermic, attractive way for producing highly "pure" hydrogen with reduced CO_2 emissions. Although the CDNG reaction was extensively studied in the last decades, the main technological drawbacks associated with catalyst lifetime and regeneration remain still unsolved [1]. Ni-based systems are the most investigated systems since they are active and stable at mild reaction conditions (T_R, 773–873 K; P_R, 0.1MPa) [2–6]. Unfortunately, their use has met some drawbacks since they are active in a very narrow window of working temperature and are unstable during oxidative treatment (burn-off with O_2/air, gasification with H_2O/CO_2) normally used for coke removal [7,8]. The cobalt-based catalysts have been object of several studies in the CDNG reaction [9,10]. At temperatures higher than 873K in CH_4 atmosphere the cobalt catalysts promote the formation of "single walled nano-tube" (SWNT) [11]. Although the Co catalysts are less active with respect to the Nickel catalysts they result to be more stable by operating at higher temperature.

In this work, Ni and Co/Al_2O_3/Silica Cloth Thin Layer Catalysts (CoAS) for Catalytic Decomposition of Natural Gas (CDNG) were investigated using a Multilayer Catalytic Reactor (MLR) [1,10]. The influence of metal loading and reaction temperature was evaluated with the aim to design a novel catalyst suitable to develop a dual-step process to produce pure hydrogen for fuel cell. The obtainment of high methane conversion level (> 80%) required reaction temperature higher than 925K and Ni based TLC samples were not found adequate since at high temperature Ni drastically deactivated by encapsulating coke formation. Irrespective of Ni loading, at temperature lower than 873K, MWCN with Ni at tip regularly formed and catalysts destroys due to the detachment of Ni particle from the carrier surface.

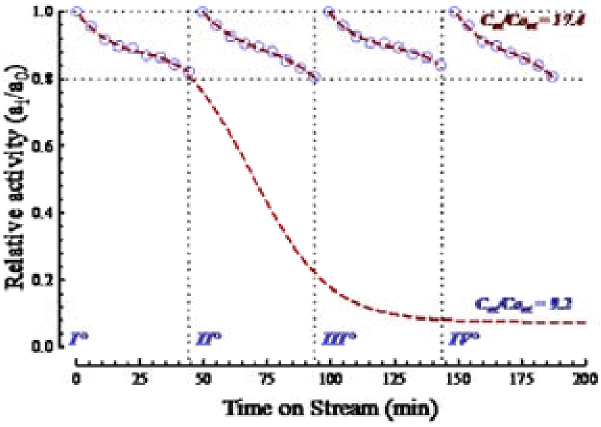


Fig. 1. Relative activity as a function of reaction /regeneration cycles: Co catalyst; Tr = 923K.

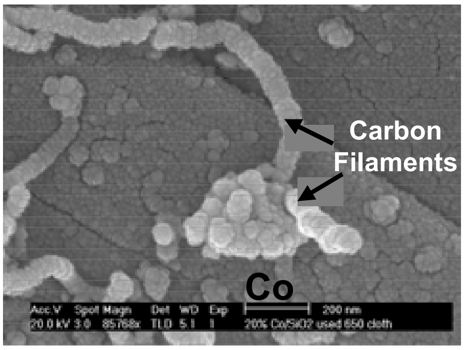


Fig. 2. Evidence of carbon filament growing mechanism on Co thin layer catalyst.

On the contrary, Co catalysts were found not so active at low temperature (< 873K) but they resulted to be very active and sufficiently stable at higher temperature (923K) and can be regenerated by oxygen treatment (see Fig.1). Iirrespective of reaction temperature investigated, on the contrary of what occur on Ni-based catalysts, on Co TLC sample due to a strong MSI filamentous coke forms with a "base" reaction mechanism (see Fig. 2) and Co particles remain well anchored on Al_2O_3 carrier. This allowed to realize a dual-step system based on CDNG reaction at 923K and regeneration at 823K in oxygen stream without any deactivation problem.

References

[1]. G. Italiano, C.Espro, F.Arena, F.Frusteri, A.Parmaliana, Stud. Surf. Sci. Catal. 162 (2006) 633.
[2]. D. Chen, R. Lødeng, A. Anundskas, O. Olsvik, and A. Holmen, Chem. Eng. Sci. 56 (2001)1371.
[3]. S. Takenaka, H. Ogihara, I. Yamanaka, K. Otsuka, Appl. Catal. A: Gen. 217 (2001)633.
[4]. B. Monnerat, L. Kiwi-Minsker, A. Renken, Chem. Eng. Sci. 56 (2001) 633.
[5]. L.B. Avdeeva, O.V. Ghoncarova, D.I. Kochubey, V.I. Zaikovskii, L.M. Plyasova, B.N.Novgorodov, S.K. Shaikhutdinov, Appl. Catal. A 141 (1996) 117.
[6]. L.B. Avdeeva, D.I. Kochubey, Sh.K. Shaikhutdinov, Appl. Catal. A 177 (1999) 43.
[7]. M.A. Ermakova, D.Yu. Ermakov, G.G. Kuvshinov, Appl. Catal. A 201 (2000) 61.
[8]. S. Takenaka, Y. Tomikubo, E. Kato, K. Otsuka, Fuel 83 (2004) 47.
[9]. T.V. Choudhary, C. Sivadinarayana, A. Klinghoffer, D.W. Goodman, Stud. Surf. Sci. Catal.136 2001) 197.
[10].G. Italiano, C. Espro, F. Arena, F. Frusteri, A. Parmaliana, Catal. Letters 124 (2008) 7.
[11].M. Wietschel, U. Hasenauer, Renewable Energy 32 (2007) 2129.

ORAL PRESENTATIONS

SECTION I

Advances in Chemical Reactors Fundamentals

Chemical Reactions Kinetics
Fundamentals of Chemical Reactors Simulation
Heat & Mass Transfer in Chemical Reactors
Hydrodynamics and CFD Studies in Chemical Reactors

REACTION KINETICS AND REACTION ENHANCEMENT FOR SOLID-LIQUID REACTIONS

Henrik Grénman, Dmitry Yu. Murzin, Tapio Salmi

Åbo Akademi University, Turku/Åbo, Finland, dmurzin@abo.fi

Dissolution kinetics of solid particles is an industrially relevant operation, for instance in hydrometallurgy, medicine, pulping, waste processing, oceanography, crystallography, ceramics and desalination technology, as well as in a number of biological and environmental precipitation processes. Not only the structural properties of the solid particles influence significantly the reaction evolution, but also the reaction media. In general, the dissolution kinetics depends on the concentration and temperature of the reactants; the transport effects and mass transfer limitations; the structural properties of particle ensembles expressed, for example, by particle-size distribution functions or surface areas.

Quantitative modelling of reactive solids in liquids is a big challenge. The reaction mechanism can be a very complex one, comprising several – often unknown – elementary steps, and the structure and structural changes of the solid material are difficult to reveal. Kinetic and mass transfer effects are coupled; to determine the intrinsic kinetics, the experiments should be free from mass transfer limitations. External mass transfer resistance can be suppressed by creating strong enough turbulence around the solid particles, but internal mass transfer effects easily remain for porous particles.

The changing surface area of solids during the reaction is very challenging and often practically impossible to measure accurately, which complicates significantly the quantitative modelling compared to homogeneous reactions.

For reactive solids, several theories have been developed to describe the structural changes of the solid material: shrinking particle model (the product material is soluble or is immediately removed from the surface), product layer model (the product remains on the surface as a porous layer causing increasing internal mass transfer resistance) and the grain model (solid material consists of non-porous grains, a raspberry-like structure) [1]. Previously, the discrimination between rival models for the solid structure was mainly based on the examination of kinetic data (weight change of the solid and/or chemical analysis of the liquid phase), but the development of microscopic techniques (SEM and TEM) and particle size analysis have opened a new perspective: the particle becomes visible and competing models can be excluded on the basis of direct observations.

It has been shown in the present work that the surface area of a solid phase (*A*) can be expressed with a generalized equation $A = \frac{aM}{\rho_P R_0} {n_0}^x n^{1-x}$, which can further be incorporated into a rate equation e.g. $\frac{dc_A}{dt} = -kA_A c_B^y$, where R_0 is the characteristic dimension of the solid particle in the beginning of the reaction (radius of a sphere or infinite cylinder, half-thickness of a slab), n_0 and n denote the amount of solid substance at t=0 and at an arbitrary reaction time, respectively. M and ρ are the molar mass and density of the solid material, respectively. The shape factor (a=1/x) is defined accordingly $a = \frac{A_P}{V_P} R_0$,where A_p and V_p are the surface area and volume of the particle.

Although reactions between solids and liquids, and more specifically dissolution processes have been intensively studied the rigorous treatment of dissolution kinetics is far from complete. In the present work the dissolution kinetics of several industrially relevant reactions (leaching of zinc from sphalerite utilizing ultrasound for reaction enhancement; dissolution of boehmite and gibbsite in sodium hydroxide) was studied. The experimental data for different cases and the results of kinetic modeling will be presented.

References

[1]. T.O. Salmi, J.-P. Mikkola, J. Wärnå, Chemical Reaction Engineering and Reactor Technology, CRC Press, 2010.

RELATION BETWEEN THE ACTIVATION ENERGY OF HETEROGENEOUS CATALYTIC REACTIONS AND THE FRACTAL DIMENSION OF CATALYST

Strizhak P.E., **Gurnyk T.M.**, **Tripolskyi A.I.**

L.V. Pysarzhevsky Institute of Phisical Chemistry, Ukrainian National Academy of Sciences, Ukraine, E-mail: pstrizhak@hotmail.com

Introduction

Characterization of catalysts in terms of fractal geometry has been found to be useful in catalytic studies [1]. Particularly, many experiments show an effect of fractal structure of a catalyst on catalytic reactions. In present study we develop a theoretical approach, which reveals a relation between the fractal dimension of catalyst and the activation energy of heterogeneous catalytic processes. The validity of the approach is confirmed by experimental results.

Theory

Catalysis at solid surface is associated with active sites. Reactants are adsorbed on the active sites forming activated complex. Formation of activated complex disturbs surface atoms reorganizing them. As a result, the reorganization of a surface, where active sites are located, may affect chemical reaction rate, namely, the activation energy. In the frame of the fractal approach introducing scaling between activation energy and fractal dimension, we derive the following relation:

$$\ln(E_a - E_0) = \ln(\pi\varepsilon) + \ln(R/r)D_F \tag{1}$$

where E_a is the activation energy of the process on the catalytic surface with fractal dimension D_F, E_0 is the activation energy for activated complex on isolated active site, ε is the reorganization energy of the surface per one atom, R is the radius of disturbed area of the surface and r is the radius of adsorbed molecule (e.g. N_2) used for the surface measurement.

Results and discussion

We performed an experimental study to verify Eq.1 studying the CO oxidation over various solids with different fractal dimensions [2,3]. According to the theoretical consideration, a plot of $\ln(E-E_0)$ against D_F for silica porous materials, which characterized by different surface fractal dimension, is presented in Fig. 1. This dependence is linear showing a good agreement between theory and experimental results. The best fit of the experimental data by Eq.1 gives the value $E_0 = 33 \pm 1$ kJ/mol. The intercept of the plot gives the value of reorganization energy of the surface per one atom (ε), equal to 8.6 ± 0.5 J/mol. Assuming that activated complex occupies only one atom of the catalyst surface, it may be estimated that 200 – 400 surface atoms are disturbed. The value $\varepsilon = 8.6$ J/mol is the average energy for all disturbed atoms of surface which participate in the active complex formation. The ratio of R/r, obtained from the slope of the plot, is equal to 15.5 ± 0.5. This value indicates that the radius of surface reorganization is almost 16 times higher than the radius of activated complex. The same correlations were found for other catalytic systems.

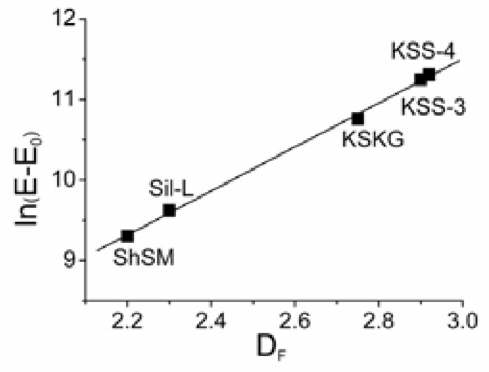


Fig. 1. The dependence of the activation energy on the fractal dimension of silica

In contrast to silica, the samples of zirconia are characterized by constant surface fractal dimension. According to Eq.1, the activation energy should be constant, which is in a good agreement with experimental results, which show $E_a = 100 \pm 5$ kJ/mol.

Conclusions

Based on fractal geometry we derive a relation (1) between the activation energy and the surface fractal dimension of a catalyst. We show that theoretical results are in a good agreement with experiments. Our approach allows to determine activation energy of activated complex and disturbance energy of catalyst surface and radius such disturbance. It provides getting additional information about heterogeneous catalytic reaction mechanism and allows separating the chemical and structural contribution of catalyst to activation energy of heterogeneous catalytic process. Our approach opens new avenues for understanding structure sensitivity in heterogeneous catalysis.

References

[1]. Rothschild W.G., Fractals in Chemistry, John Willey & Sons, New York, 1998, p.235
[2]. Trypolskyi A.I., Gurnyk T.M., Strizhak P.E. Chem. Phys. Lett. 2008, 460, p.492-494
[3]. Strizhak P.E., Gurnyk T.M., Trypolskyi A.I. Trends in Phys. Chem. 2008, 13, p,55-65

COMPARISON OF CHEMICAL AND ENZYMATIC CATALYSIS: KINETIC STUDIES IN BENCH-TOP PACKED BED REACTOR

Pečar D., Goršek A.

University of Maribor, Faculty of Chemistry and Chemical Engineering,
Smetanova 17, SI-2000 Maribor, Slovenia,
darja.pecar@uni-mb.si, andreja.gorsek@uni-mb.si

Most traditional chemical catalysts can significantly improve economic potential of an industrial fine chemicals production by increasing the reaction rates. However, their applicability in modern organic synthesis is limited due to low selectivity and environmental issues. In contrast, enzymes known as biocatalyst are usually highly selective and therefore enable development of novel and chemically complex reaction pathways for efficient tailored product production. Nowadays, they are widely used commercially, for example in the modern sustainable detergent, food and brewing as well as pharmaceutical industries. However, preparative application of enzymes can cause some technical and especially economical annoyances. They are water soluble which makes them hard to recover and some products can inhibit the enzyme activity. Therefore, enzymes are usually immobilized. Generally, the biocatalysis is preferable to the chemical one, because of mild process conditions, non colored products, efficiency and environmental acceptability [1, 2].

In the present study kinetic parameters of well known chemical and biological reaction, performed in bench-scale packed bed reactor, have been determined and compared. The sucrose hydrolysis was chosen for investigation because it has applications in several industrial processes, it is safe and environmentally friendly. This organic synthesis produces an equimolar mixture of fructose and glucose dominated invert sugar [3]. The product can be produced by traditional chemical conversion or by bioconversion using the enzyme invertase as biocatalyst. Amberlite IR 120 was used as a chemical catalyst and immobilized enzyme invertase as a biological one. The influence of reaction mixture temperature and volume flow rate on conversion was investigated in the case of chemical synthesis. The same process parameters were studied also for alternative enzymatic synthesis, except that enzyme concentration was added as bioproces parameter.

All experiments were performed in a laboratory bench-top packed bed reactor system. The reactor was equipped with the FTIR based ReactIR^{TM} iC10 analysis system (Mettler Toledo, model: 910–7002), which was used as PAT tool for the real time monitoring of sucrose-glucose-fructose molar concentration profiles. As an example the FTIR spectra collected during one selected experiment is presented in Fig. 1. It can be clearly seen that the intensity of the broad peak (absorbance, A) within the wavenumber range, ν = (978–1096) cm^{-1} increases over the reaction time. After a certain period of time, depending on experimental conditions, stady state is formed.

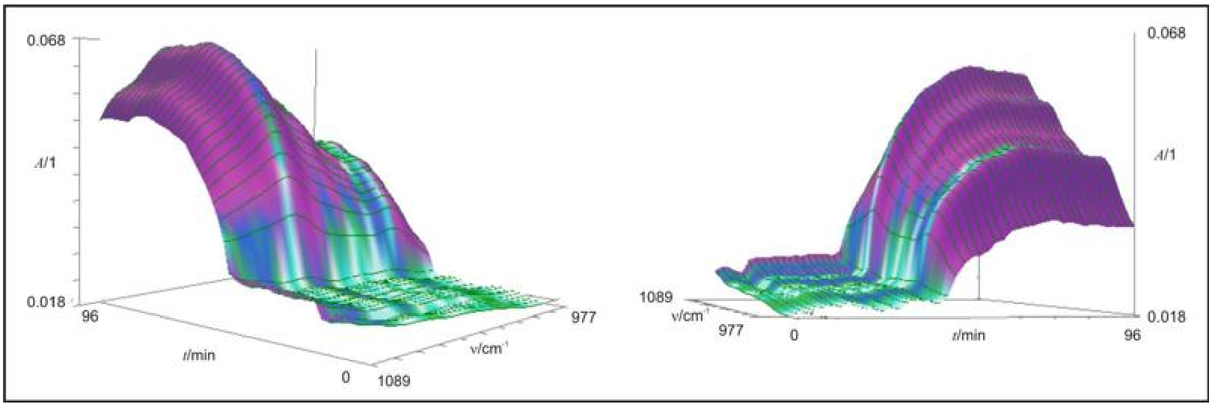


Figure 1: Waterfall plots of FTIR spectra during the sucrose hydrolysis at reaction mixture temperature, ϑ = 50 °C and volume flow rate, q_V = 7 mL·min^{-1} (shown with different angel of sight).

The FTIR spectra were transformed to the real-time molar concentration profiles of sucrose considering peak areas treatment of the corresponding peak with the two point base line correction. The concentration of sucrose, glucose and fructose in the reaction mixture was determined using calibration curve.

Data obtained from the experiments yielded, through application of mathematical modeling, kinetic information such as rate constant for chemical reaction, Michaelis-Menten parameters for enzymatic reaction, activation energy and the reaction rates for both reactions. All values were compared to previously published ones. Determining reaction kinetics is one of the most crucial development step in reactor system design. In order to achieve the highest accuracy and validity regarding kinetic measurements in the chemical, biochemical, food and pharmaceutical industries high-quality and up-to date equipment is necessary. With presented analysis it was verified that our bench-top packed bed reactor is adequate to perform kinetic studies, particularly if it is used in combination with FTIR, one of the most powerful, proven and widely used PAT tool. Also the advantages of enzymatic reaction were exposed.

References

[1]. L.D.S. Marquez, B.V. Cabral, F.F. Freitas, V.L. Cardoso, E.J. Ribeiro, Journal of Molecular Catalysis B: Enzymatic, 2008 51 86-92.

[2]. S. Kumar, V. S. Chauhan, P. Nahar, Enzyme and Microbial Technology, 2008 43 517-522.

[3]. A. C. S. de Almeida et. al., Electronic Journal of Biotechnology, 2005, 8, 55-62.

NONLINEAR PHENOMENA DURING METHANE OXIDATION OVER METALLIC CATALYSTS: EXPERIMENT AND MATHEMATICAL MODELLING

Slinko M.M.[1], Peskov N.V.[2], Bychkov V.Yu.[1], Tyulenin Yu.P.[1], Korchak V.N.[1]

[1]*Semenov Institute of Chemical Physics RAS, Moscow, Russia*
[2]*Department of Computational Mathematics & Cybernetics,*
Moscow State University, Moscow, Russia

Catalytic oxidation of alkanes over metallic catalysts is important in a wide variety of industrial processes including catalytic partial oxidation into syngas for fuel-rich feeds. For the design and safe operation of this process a precise knowledge of a reaction mechanism is necessary. Recently nonlinear behaviour has been observed during C_1-C_3 oxidation over metallic catalysts [1]. Much information about a reaction mechanism can be obtained from the study and mathematical modelling of the oscillating catalytic reactions [2]. The present work summarises experimental results and modelling studies concerning an oscillatory behaviour during methane oxidation over Ni and Pd catalysts.

The application of thermographic (TG) analysis in combination with on-line mass-spectrometry and visual observations of the catalyst surface during oscillations provided the definite proof that the origin of the oscillatory behaviour in both systems was connected with the periodical oxidation-reduction of a catalyst. However there are many differences between oscillations during methane oxidation over Ni and Pd catalysts. Oscillations over Ni catalysts were detected at higher temperatures (650-900°C). During oscillations the variation of the selectivity of the process has been detected. The oxidized state was characterised by lower activity of methane oxidation with maxima in CO_2 and H_2O concentrations, while the degree of methane conversion is much greater on the reduced surface, where mainly products of partial methane oxidation CO and H_2 were produced.

The mathematical model of the oscillatory behaviour during methane oxidation over Ni catalysts was derived in the mean field approximation. It simulated qualitatively the main properties of the oscillatory behaviour observed experimentally during the reaction of methane oxidation over Ni catalysts. It was demonstrated that thermokinetic oscillations in this system originated due to periodic oxidation-reduction of the catalyst surface, the variation of the selectivity of the process and the competition of reactants for the free active sites.

No variation of the selectivity and only the products of the total oxidation were detected during methane oxidation over Pd catalysts indicating an essentially different mechanism of oscillations in comparison with Ni and Co catalysts. Under certain conditions the unusual behaviour, namely the phase shift between oscillations of CO_2 and H_2O concentrations was observed.

The application of TG analysis in combination with on-line mass-spectrometry allowed to identify the variation of the Pd state during one cycle of the oscillations and to correlate various states of Pd with a catalytic activity. It was demonstrated that the nature of the oscillations was connected not only with periodic oxidation and reduction of a Pd catalyst as suggested in earlier studies [3], but also carbon deposition-removal played an essential role in the mechanism of the oscillations. It was shown that exactly the accumulation of carbon in a Pd catalyst was the origin of the antiphase oscillations of CO_2 and H_2O concentrations.

The mathematical model was developed, which can simulate the dynamic behaviour of the surface coverages, the concentrations of dissolved carbon and oxygen, catalyst temperature and partial pressures of reactants. It was demonstrated that the reduction-oxidation processes of the Pd catalyst could lead to the appearance of the reaction rate self-sustained oscillations. Different modifications of the model, considering lateral interactions in the adlayer and/or carbon diffusion in the deep layers of the catalyst will be discussed. It will be demonstrated how the properties of the observed experimentally oscillations, namely the phase shift between the oscillations of the reaction products CO_2 and H_2O can help in the discrimination of the mathematical models.

Aknowlegement

This work was supported by the Russian Foundation for Basic Researches (grant N 08-03-00364.

References

[1]. V.Yu. Bychkov, Yu.P. Tyulenin, M.M. Slinko, V.N. Korchak, Surface Science 603 (2009) 1680.

[2]. M.G. Slinko “Catalysis in Industry” 1 (2006), 5.

[3]. X.L. Zhang, C.S.-M Lee, D.M.P. Mingos and D.O. Hayward, Appl. Catal. A: Gen., 240 (2003) 183.

SPECIFICITY OF THE OSCILLATIONS PERFORMANCE OVER THE FLEXIBLE SURFACES OF THE METAL NANOPARTICLES: MONTE-CARLO APPROACH

Vladimir Elokhin[1,2], Konstantin Kalgin[2,3], Evgenii Kovalyov[1], Andrei Matveev[1,2], Vladimir Gorodetskii[1]

[1]Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia, elokhin@catalysis.ru
[2]Novosibirsk State University, Novosibirsk, Russia
[3]Institute of Computational Mathematics and Mathematical Geophysics SB RAS, Novosibirsk, Russia

The properties of the metal nanoparticles serving often as commercial catalysts differ significantly from those of similar systems with large dimensions. Particularly the shape and the surface morphology of supported nanoparticles are not fixed (flexible) and can appreciably change in the course of reaction. Besides, spillover by diffusion of reactants between the particle and its support can induce changes in catalytic behavior. The theoretical models aimed at the simulating of catalytic properties of nanometer scale particles requires the use of atomic-scale computer simulations taking into account the intrinsic heterogeneity of nanoparticles. The most effective tool for the simulation of the spatiotemporal dynamics of adsorbed species on the flexible catalytic surfaces are now the stochastic methods based on the Monte-Carlo technique permitting one to obtain qualitatively new results [1-3].

We studied the model of oscillatory dynamics of the CO + O_2 reaction over the supported Pd nanoparticles by means of Monte-Carlo technique. For that we combine the kinetic Monte-Carlo (kMC) approach to model the CO + O_2 reaction over the Pd(110) single crystal [4] and the stochastic model for the imitating the supported nanoparticle with dynamically changing shape and surface morphology [5]. According to [6,7], it is necessary to take into account the contribution of CO_{ads} diffusion over the support onto the active metal particle surface (reverse spillover) giving the additional source of CO_{ads} flux to the particle through its perimeter. The amount of CO_{ads} reaching a nanoparticle is defined through the collection zone, which depends on the mean diffusion length of CO_{ads} on the support and on the density of particles.

The following mechanism of the reaction [4] has been used for the simulations

1) $O_{2(gas)} + 2* \rightarrow 2O_{ads}$;

2) $CO_{gas} + * \leftrightarrow CO_{ads}$;

3) $CO_{ads} + O_{ads} \rightarrow CO_{2(gas)} + 2*$;

4) $O_{ads} + *_{v} \rightarrow [*O_{ss}]$;

5) $CO_{ads} + [*O_{ss}] \rightarrow CO_{2(gas)} + 2* + *_{v}$;

6) $CO_{gas} + [*O_{ss}] \rightarrow [CO_{ads}*O_{ss}]$;

7) $[CO_{ads}*O_{ss}] \rightarrow CO_{2(gas)} + * + *_{v}$,

where $*$ and $*_v$ are the active centers of the surface and subsurface layers, respectively. CO can adsorb both over the surface of particle and the support (desorption coefficient of CO_{ads} from the support was assumed several times higher than that from the Pd particle) and then diffuse through the support (intensity of diffusion was assumed several times higher than that over the Pd particle) to the Pd particle; oxygen can adsorb only on the available centers of the palladium particle, preferably on the terraces.

The influence of both reaction parameters (rate coefficients and diffusion intensity) and particles characteristics (size, degree of roughening, etc.) on the oscillation behavior and pattern formation has been studied. Decreasing of the particles size to less than ~ 30×30 active centers (depending on the chosen set of parameters) leads to the disappearing of oscillations. The reasons for this phenomenon are the following: (i) decreasing of the particles size leads to the roughening (increasing of the defects concentration) of its surface and, hence, to the deficit of the available centers for oxygen adsorption; (ii) the influence of the additional flux of CO_{ads} from the perimeter shifts the interval of oscillations to the higher values of the oxygen partial pressures. The presence of CO_{ads} spillover determines the character of concentration waves over the surface of Pd nanoparticle – oxygen wave propagates from the central region of the particle to the perimeter, and the CO_{ads} wave moves from the perimeter, always enriched by CO_{ads}, to the centre of the particle. In the case when the collection zones [6,7] overlap (the density of the particles on the support is high) the synchronization of oscillations between neighboring oscillators (nanoparticles) due to CO_{ads} diffusion over the support seems to be possible. The presence of CO_{ads} spillover over the support can manifest as size-dependent reactivity of the supported catalysts.

References

[1]. Zhdanov V.P., Kasemo B. *Surf. Sci. Rep.*, **2000**, 39, 25-104.
[2]. Zhdanov V.P. *Surf. Sci.*, **2002**, 500, 966-985.
[3]. Elokhin V.I., Myshlyavtsev A.V. In: *Dekker Encyclopedia of Nanoscience and Nanotechnology*, 2nd Ed., Vol. II. C.I. Contescu and K. Putyera, Eds.; Taylor & Francis: New York, **2009**; pp. 782-793.
[4]. Latkin E.I., Elokhin V.I., Matveev A.V., Gorodetskii V.V. *J. Molec. Catal. A, Chemical*, **2000**, 158*,* 161-166.
[5]. Kovalyov E.V., Elokhin V.I., Myshlyavtsev A.V. *J. Comput. Chem.,* **2008**, *29*, 79-86.
[6]. Henry C.R. *Surf. Sci. Rep.*, **1998**, 31, 231-325.
[7]. Boudart M. *Topics in Catalysis,* **2000,** 13, 147-149.

Acknowledgements This work was supported by the RFBR Grant # 08-03-00454.

OP-I-6

TRENDS IN BISTABILITY DOMAINS OF CO OXIDATION ON TRANSITION METALS CALCULATED FROM FIRST PRINCIPLES

Sheintuch M., German E., Nekhamkina O.

Dept. of Chemical Engineering, Technion-I.I.T., Haifa, 32000
cermsll@tx.technion.ac.il

A century of research into CO oxidation revealed a plethora of unique phenomena, but still many questions remain open in deriving a predictive kinetic model for the most popular catalysts. The main qualitative phenomena associated with this and similar reactions are the negative-order kinetics, multiple solutions (bistability), oscillatory behavior and spatiotemporal patterns. It is important, therefore, to suggest a methodology for finding its kinetic parameters and overall rate from first principles, when possible.

We consider two models of CO oxidation on group VIII metals: both include CO adsorption and desorption and surface reaction:

$$\mathrm{CO} + \sigma \overset{k_1}{\underset{k_{-1}}{\longleftrightarrow}} \mathrm{CO_s}; \qquad \mathrm{CO}_s + \mathrm{O}_s \xrightarrow{k_3} \mathrm{CO_2} + 2\sigma \tag{1}$$

While for oxygen adsorption we use either a two-step indirect (a) or direct (b) model:

$$\text{(a)}\ \mathrm{O_2} + \sigma \overset{k_{2M}}{\underset{k_{-2M}}{\longleftrightarrow}} \mathrm{O}_{2s}; \mathrm{O}_{2s} + \sigma \overset{k_t}{\underset{k_{-t}=0}{\longleftrightarrow}} 2\,\mathrm{O}_s; \quad (b) \qquad \mathrm{O_2} + 2\,\sigma \overset{k_2}{\underset{k_{-2}=0}{\longleftrightarrow}} 2\,\mathrm{O_s} \tag{2}$$

The first model can be reduced approximately to the second one which is better amenable to analytical treatment and predicts a rate (R_{CO}) vs. CO partial pressure (P_{CO}) diagram as a clockwise hysteresis loop (Fig. 1). Bistabilty has been observed and modelled for many catalytic reactions on either single crystals of Pt, Pd, Ir under high vacuum conditions using molecular beam or in atmospheric-pressure studies on polycrystalline Pd and Pt.

In the present study we employ our previous results for the elementary steps rate constants of the models described above. Three of them, the rate constants of CO oxidation (k_3), of O_2 dissociative adsorption (k_t) and of CO diffusion constant ($k_{A,dif}$) were calculated using the analytical approach searching for the saddle point (SP) on semi-empirical adiabatic potential energy surface (APES)[1-4]; other rate constants were estimated using the standard theory of rate processes. The APES is constructed from two diadiabatic surfaces U_i and U_f characterizing the potential energies of reactants and products corresponding to the Fermi energy of electrons in a metal

$$U_{ad}^{g} = 1/2[U_i + U_f - \sqrt{(U_i - U_f)^2 + 4V^2}] \quad (4)$$

where *V* is an empirical function providing a smooth transition from the region of the initial potential well to the region of the final one. Two sets of coordinates, the geometris of the adsorbed molecule(s) and the rearranged surface geometry are introduced to describe most significant changes as reactants adsorbed transfer into products. We review the main ideas of this approach.

Using the kinetic information (Fig. 1) for 5 metals (Pt, Pd, Ir, Rh, Ru) we draw and compare the bistability domain for either atmospheric pressure or for high-vacuum conditions. The obtained results are compared with available experimental results. We also show its asymptotic limits: the rate constant (k_3) is sufficiently large as not to affect the rate. We also present initial results of a similar approach for predicting oscillatory behavior from first principles.

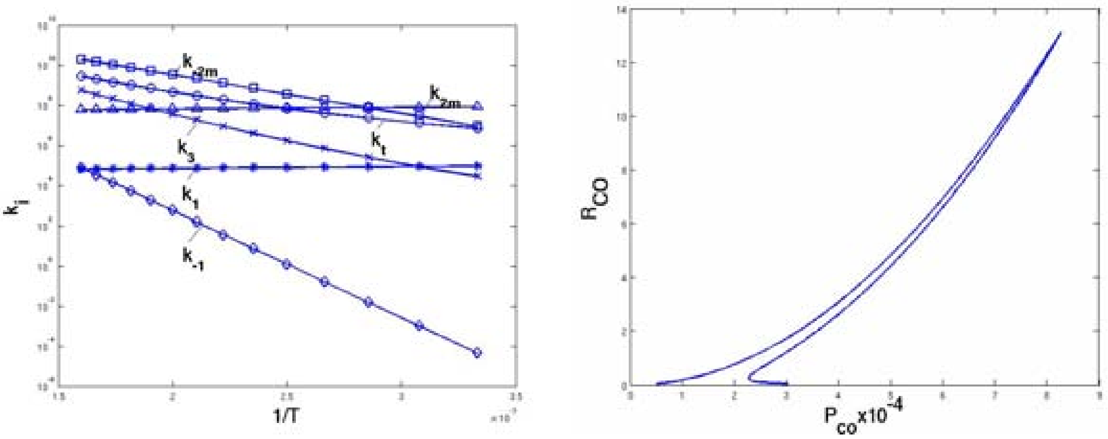


Fig. 1. Temperature dependence of the rate constants calculated from basic principles for Pt (left, k_1 for 1mbar, k_{2M} for 1 bar) and the predicted hysteresis rate curve at 550K for Pd(right, P_{O2}=1bar).

References

[1]. E. D. German, A. M. Kuznetsov, M. Sheintuch, Surf. Sci. **2004**, 554, 159, 170.
[2]. E. D. German, A. M. Kuznetsov, M. Sheintuch, Chem. Phys**. 2006**, 324, 129.
[3]. E. D. German, M. Sheintuch, J. Phys. Chem., C **2007**, 111, 9184.
[4]. E. D. German, M. Sheintuch, A. M. Kuznetsov, J. Phys. Chem., C **2008**, 112, 15510.

NON-STEADY-STATE CATALYST CHARACTERISATION WITH THIN-ZONE TAP EXPERIMENTS

Evgeniy Redekop[1], **Gregory Yablonsky**[2], **John T. Gleaves**[1], **Xiaolin Zheng**[1], **Denis Constales**[3]

[1]*EECE Dept., Washington University in Saint Louis, MO, er2@cec.wustl.edu*
[2]*Parks College, Department of Chemistry, Saint Louis University, MO*
[3]*Department of Mathematical Analysis, Ghent University, Gent, Belgium*

Introduction

The non-steady-state kinetic characterization of the heterogeneous catalysts is very informative for elucidating the structure-activity relationships and measuring the reaction rate, R(t), as a function of gas composition, C(t), which is vital for successful catalyst development and improvement of industrial catalytic technologies. The Temporal Analysis of Products (TAP) reactor system is an advanced instrument for the kinetic study of the heterogeneous catalysts which bridges the material and pressure gaps between applied kinetics and surface science [1]. In this work we develop a kinetically model free framework for non-steady-state TAP data analysis using Y-Procedure, the algorithm for the reconstruction of R(t) and C(t) from the exit fluxes recorded in a Thin-Zone TAP experiment [2]. The Y-Procedure was applied to experimental data obtained for carbon monoxide (CO) oxidation catalyzed by silica supported gold nanoparticles. The characteristic patterns in the rate/concentration data obtained in the experiment are compared to the patterns modeled by a simple reversible adsorption on the surface.

Thin Zone TAP experiments and Y-Procedure

In the Thin Zone (TZ) configuration of the TAP reactor the thickness of the catalytic zone is made small in comparison with the reactor length (Fig. 1) to ensure that the concentration and temperature gradients within the catalytic material can be neglected for conversions as high as 75 % in a non-steady-state experiment [3]. Recently, the Y-Procedure was developed for the reconstruction of the gas concentrations and the surface reaction rates from the exit flux measured in a TZ TAP experiment [2]. Mathematically, the Y-Procedure is based on the Laplace domain solution of the diffusion equation for the inert zones in the TZ TAP reactor. The numerical algorithm utilizes the equivalent of this solution in the Fourier domain. The key feature of the Y-Procedure is that the non-steady-state gas concentrations and the reaction rates are extracted from the experimental data without any *a priori* assumptions about the reaction mechanism.

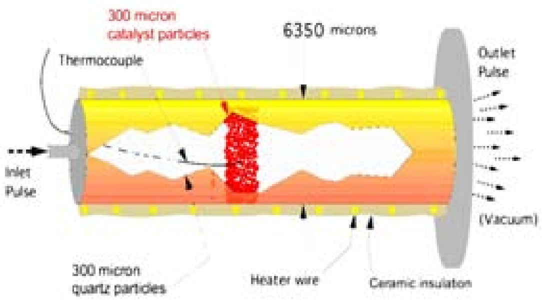


Figure 1. Thin Zone TAP microreactor.

Results

Previously, the Y-Procedure was introduced and illustrated by just one example - the first order reaction on the surface [2]. In this work, the Y-Procedure for the first time was applied to a range of more complex cases including both, model mechanisms (irreversible coverage dependent adsorption, reversible adsorption, Eley-Rideal, Langmuir-Hinshelwood) and real experimental data (CO adsorption on silica supported gold nanoparticles). The results indicate that the Y-Procedure can be used efficiently to extract the gas concentration and the reaction rate from the experimentally observed exit flux data after appropriate filtering. As an example, Fig. 2a depicts a 3D plot of the CO adsorption reaction rate, R(t), versus the CO gas concentration, C(t), and the amount of CO on the surface, S(t), calculated from the reaction rate. Comparison with the simulation of simple reversible CO adsorption depicted on Fig. 2b shows that the general pattern in the non-steady-state kinetics of CO adsorption on the catalyst is similar to that of the model reversible adsorption (closed loop). Nevertheless, there are considerable deviations of the experimental pattern from the model one. For example, the experimental trajectory does not lay in a single plane as the model trajectory does. This behavior suggests more complex interaction of the CO with the surface of the gold catalyst than the simple reversible adsorption.

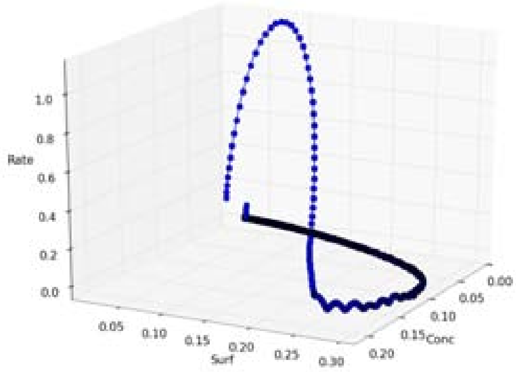


Figure 2a

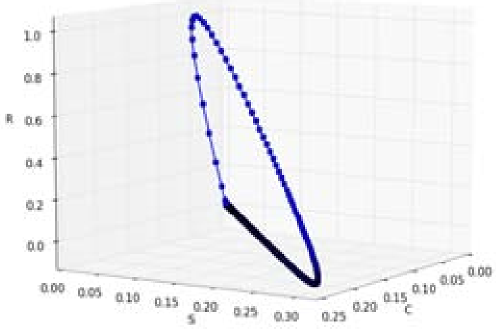


Figure 2b

Conclusions

The Y-Procedure was applied to a number of model mechanisms and to the real experimental data. The TZTR TAP experiment with Y-Procedure analysis can serve as a basis for the kinetically model free non-steady-state catalyst characterization.

References

[1]. John T. Gleaves, Gregory S. Yablonsky, Xiaolin Zheng , Rebecca Fushimi, Patrick L. Mills, Temporal analysis of products (TAP)–Recent advances in technology for kinetic analysis of multi-component catalysts, J. Mol. Catal. A: Chem., 2010, 315, 108-134.

[2]. Sergiy O. Shekhtman, Gregory S. Yablonsky, John T. Gleaves and Rebecca R. Fushimi, Thin-zone TAP reactor as a basis of “state-by-state transient screening”, Chem. Eng. Sci., 2004, 59, 5493-5500.

[3]. G.S. Yablonsky, D. Constales, S.O. Shekhtman, J.T. Gleaves, The Y-procedure: How to extract the chemical transformation rate from reaction–diffusion data with no assumption on the kinetic model, Chem. Eng. Sci., 2007, 62, 6754-6767.

TRANSIENT KINETIC STUDIES OF DRY REFORMING OF METHANE OVER Pt/PrCeZrO CATALYST

Vladislav Sadykov[1,2], Nataliya Sazonova[1], Elena Gubanova[1], Svetlana Pokrovskaya[1,2], Nataliya Chumakova[1,2], Alexey Bobin[1,3], Yves Schuurman[3], Claude Mirodatos[3]

[1]Boreskov Institute of Catalysis SB RAS, 630090, pr. Lavrentieva 5,
Novosibirsk, Russia, pokrov@catalysis.ru
[2]Novosibirsk State University, 630090, Pirogova 2, Novosibirsk, Russia
[3]Institut de Recherches sur la Catalyse et l'Environnement de Lyon,F-69626
Villeurbanne cedex, France

Ever-growing interest to the dry reforming of methane (DRM) is connected with the possibility to convert two greenhouse gases into syngas with H_2/CO ratio close to the most suitable for synfuels production, and the task arises to develop active and stable catalysts for both environmental and industrial applications. Pt/ZrO_2 catalysts were shown to be more attractive systems in this process than Ni-based catalysts [1,2]. DRM studies over Pt/LnCeZrO catalysts (where Ln = La, Gd, Pr) revealed that activity and stability to coking increase in the order La < Gd < Pr correlating with lattice oxygen mobility [3]. This paper presents the results of transient kinetic studies aimed at elucidating the main factors controlling the catalytic properties and stability of Pr-doped catalyst in DRM at short contact times.

Experimental and modeling. Dispersed complex oxide $Pr_{0.3}Ce_{0.35}Zr_{0.35}O_x$ was prepared via Pechini route. The complex oxides were supported on the walls of triangular fragment of α-Al_2O_3 monolith with one straight channel, Pt (1.4 wt.%) was loaded from a H_2PtCl_6 solution by incipient wetness impregnation [4]. Transient kinetic experiments were carried out using quartz reactor of 4-6 mm ID with a separate catalytic fragment [3]. Before reactions, samples were pretreated at 700°C in stream of O_2. Reaction mixture was fed to the oxidized catalyst with CH_4 concentration of 7% vol. and CH_4:CO_2 ratio 1:1 at temperature 750°C and contact time 4.7-8 ms.

The mathematical model of processes in such a catalytic system was developed that accounts for the conversion of oxygen-containing species on the catalyst surface by reaction steps and the surface/near surface mobility of oxygen. On the base of the software developed a number of computational runs were performed at process parameters corresponding with the experimental transients to characterize the catalyst structure and evaluate the rates of main catalytic stages.

Results and discussion. It was revealed that for oxidized catalysts DRM occurs generally via the associative route including interaction of activated CH_x fragments with carbonates stabilized by cationic Pt forms at Pt-support interface. This is certified by concomitant appearance of H_2 and CO in 1:1 ratio at the reactor outlet after switch from He stream to CH_4+CO_2 for the first 20-30 s of transients. Progressive reduction of these cationic species by reaction feed decreases activity in CH_4 reforming while accelerating reverse water gas shift reaction catalyzed only by Pt^o, thus progressively decreasing H_2/CO ratio in products. This process is counteracted by the surface oxygen mobility supplying oxygen atoms to reduced Pt centers thus providing their reoxidation, while generating surface oxygen vacancies for CO_2 dissociation.

Modeling of the experimental transients with a due regard for the reaction steps occurring on the cationic forms of Pt, surface carbonates formation/consumption, Pt-support oxygen spillover, and oxygen bulk diffusion was carried out. The key characteristics of the catalyst (the number of oxide surface active sites, Pt surface concentration, characteristic length of oxygen diffusion) determined on the base of computational results agree with values independently estimated by XPS, FTIRS of adsorbed CO methods, and oxygen isotope exchange. The kinetic parameters of basic reaction steps occurring on this catalyst and the rates of surface/near surface oxygen mobility were evaluated by fitting the kinetic transients.

Conclusion. Combination of experimental research and computational analysis allowed to determine important role of the cationic forms of Pt and oxygen lattice mobility in catalytic properties of Pr-doped catalyst in DRM and to obtain the quantitative estimation of catalyst structure characteristics and the rates both of the lattice oxygen diffusion and main stages of the catalytic reaction.

References

[1]. A.M. O'Connor, Y. Schuurman, J.R.H. Ross, C. Mirodatos, Cat. Today **2006**, 115, 191-198

[2]. M. Garcia-Diegues, I.S.Pieta, M.C. Herrera, M.A.Larrubia, I.Malpartida, L.J. Alemany, Cat. Today **2010**, 149, 387

[3]. N.N. Sazonova, V.A. Sadykov, A.S. Bobin, S.A. Pokrovskaya, E.L. Gubanova, C. Mirodatos, React. Kinet. Catal. Lett. **2009,** 98, 35-41.

[4]. E.L. Gubanova, A.C. Van Veen, C. Mirodatos, V.A. Sadykov, N.N. Sazonova, Russ. J. General Chem. **2008**, 78, 2191.

Acknowledgements

This work was financially supported by RFBR–CNRS Project 09-03-93112, OCMOL FP7 Project and SB RAS Interdisciplinary Integration Project 107.

A REDOX KINETICS FOR THE PARTIAL OXIDATION OF O-XYLENE ON V_2O_5/TIO_2 CATALYSTS

López-Isunza F.

Departamento de Ingeniería de Procesos e Hidráulica, Universidad Autónoma Metropolitana-Iztapalapa. Av. San Rafael Atlixco 186, México 09340, D.F.
felipe@xanum.uam.mx

The redox mechanism proposed by Mars & van Krevelen [1] has been used to describe the kinetics for the partial oxidation of some hidrocarbons on mixed-oxide catalysts. It has been shown that this mechanism reveals some inconsistencies [2], however they may disapear if one considers that in most of the intermediary steps of the partial oxidation, not one but two adjacent “oxidised” sites [3] participate, contrary to previous reports [1, 4-6]. In this work a kinetic model based on the redox mechanism is developed based on the ideas of previous works [3, 4], and the kinetic parameters obtained by simulations using a transient CSTR model are tunned to predict some observations from the partial oxidation of o-xylene in an industrial-scale fixed bed catalytic reactor [7] and from preliminary temperature data from a CSTR (Berty) system.

The proposed kinetics is as follows:

(1) $A + 2\theta o \Rightarrow B + H_2O + 2\theta r$

(2) $B + \theta o \Rightarrow C + \theta r$

(3) $C + 2\theta o \Rightarrow D + H_2O + 2\theta r$

(4) $D + 2\theta o \Rightarrow E + H_2O + 2\theta r$

(5) $E + 2\theta o \Rightarrow F + H_2O + CO + 2\theta x$

(6) $A + 2\theta o + 8\,O_2 \Rightarrow 3CO + 4CO_2 + 5H_2O + 2\theta x$

(7) $E + 2\theta o + 7\,O_2 \Rightarrow 2CO + 5CO_2 + 2H_2O + 2\theta x$

(8) $F + 2\theta o \Rightarrow H_2O + 2\theta y$

(9) $2\theta r + O_2 \Leftrightarrow 2\theta o$

(10) $CO + \theta o \Rightarrow CO_2 + \theta r$

(11) $2\theta x + O_2 \Rightarrow CO_2 + 2\theta r$

(12) $2\theta y + O_2 \Rightarrow 2CO_2 + 2CO + 2\theta r$

Where: $A=C_8H_{10}$ (o-Xylene = OX); $B=C_8H_8O$; $C=C_8H_8O_2$; $D=C_8H_6O_2$; $E=C_8H_4O_3$ (Phthalic Anhydride = PA); $F= C_4H_2O_3$ (Maleic Anhydride = MA); θo and θr are oxidised and reduced sites, and θx and θy are lump adsorbed hydrocarbon species [3] that either remained adsorbed or go to complete oxidation, depending on temperature conditions, and only reaction (9) is reversible. One of the main objections with respect to the kinetics published so far [5, 6] is that the production of MA and the accumulation of adsorbed species are not described. The proposed model accounts for MA formation and the adsorbed lumped species. Figure 1 shows model prediction of temperature and composition from the CSTR for different ratios of catalyst mass for a constant flow of air at different temperatures. The kinetic parameters obtained from the CSTR simulations are tunned to predict observed temperature profiles from a 2.6 m length and 2.54 cm in diameter fixed-bed reactor packed with 0.82 mm spheres of externally deposited V_2O_5/TiO_2 catalyst [7] operating at typical industrial conditions, and this comparison is shown in figure 2. An important aspect of this prediction can be observed in terms of the wide of the predicted temperature profile wich is comparable in magnitude to the observed one, contrary to most predictions. The corresponding concentration profiles in the reactor for OX and PA and those for oxidized, reduced and lump adsorbe species are shown in figures 3 and 4. It has been observed that the temperature and composition profiles change with time (as shown in figure 5) due to slow but gradual accummulation of adsorbed species and to reversible deactivation, which can be partially removed with air in the absence of reaction [7]; this can also be predicted with the proposed kinetic model, as shown in figure 6, when using kinetic parameters that described a rather very rapid accumulation of adsorbed species. To be able to adequately describe the moving temperature and reaction fronts in the fixed bed reactor model, the methods of orthogonal collocation (radial) and orthogonal collocation on finite elements (axial) were used together with a 4th order Runge-Kutta method. Four interior collocation points were used in the radial coordinate and 40 elements in the axial coordinate with 4 interior points for each element.

References

[1]. Mars P. & D.W. van Krevelen: Chem. Eng. Sci. Suppl. (**1954**) 3, 41-59.

[2]. Vannice M.A. Catalysis Today (**2007**) 123, 18-22.

[3]. Haber J., R. Tokarz & M. Witko: in New Developments in Selective Oxidation II. Cortés Corberán & Vie Bellón Editors (**1994**).

[4]. Dias C.R., M.F. Portela & G. Bond: Journal of Catalysis (**1996**)164, 267-287.

[5]. Calderbank P.H. et al.: Chem. Eng. Sci. (**1977**) 32, 1435-1443.

[6]. Skrzypek J. et al.: Chem. Eng. Sci. (**1985**) 40, 611-620.

[7]. F. Lopez-Isunza, PhD Thesis, Imperial College, London UK (**1983**).

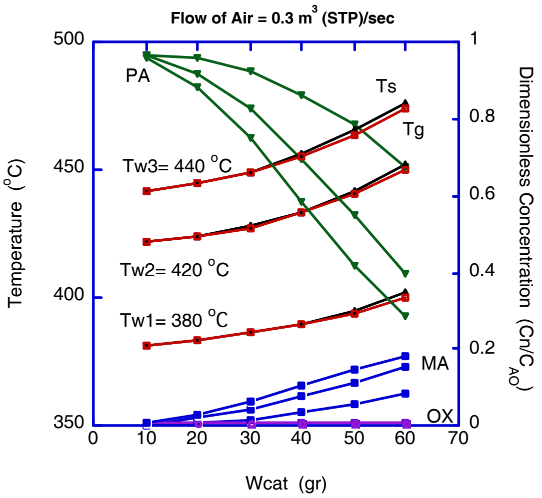


Figure 1. Calculations from the CSTR

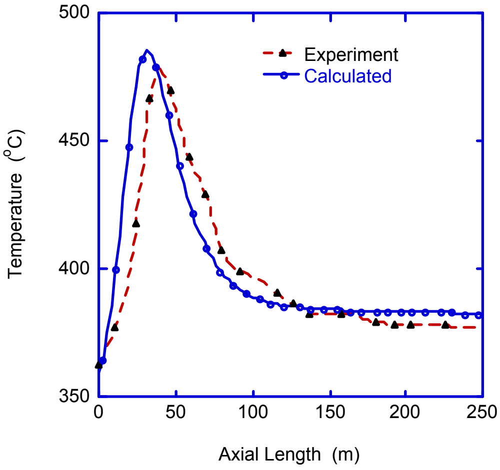


Figure 2. Comparison of temperature profiles

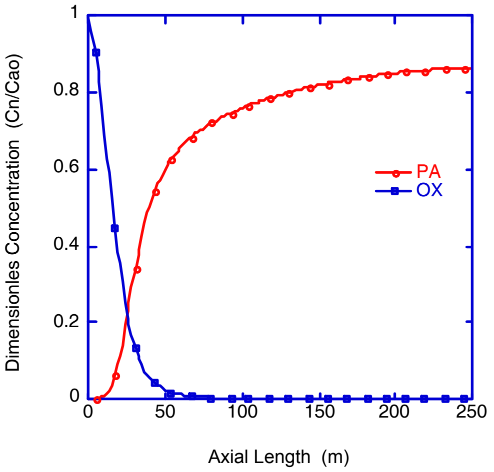


Figure 3. Predicted concentration profiles

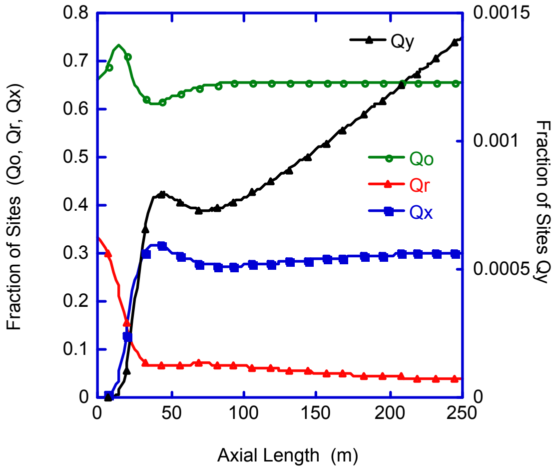


Figure 4. Predicted concentration of fraction sites

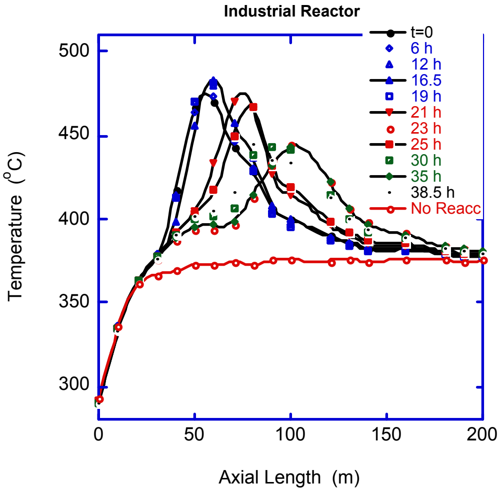


Figure 5. Evolucion of temperature profiles in the industrial reactor after 38.5 h of continuous operation

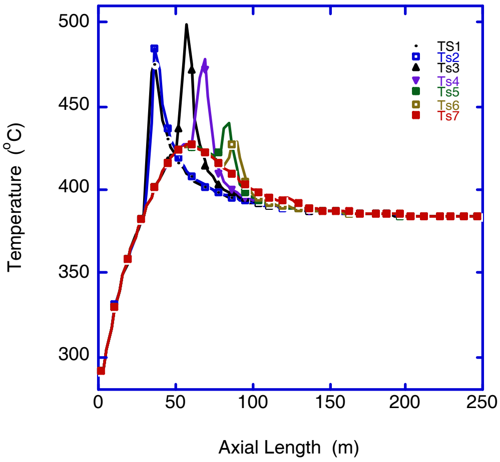


Figure 6. Predicted evolucion of temperature profiles in the reactor

OP-I-10

SINGLE-PHASE FLUID FLOW DISTRIBUTION AND HEAT TRANSFER IN MICROSTRUCTURED REACTORS

Evgeny V. Rebrov and Jaap C. Schouten

Department of Chemical Engineering and Chemistry,
Eindhoven University of Technology,
P.O. Box 513, 5600 MB Eindhoven, The Netherlands,
e.rebrov@tue.nl

Single-phase microreactors and micro heat-exchangers are widely used in industrial and scientific applications. Over the course of the past two decades, many conflicting publications with the results on the validity of classical macroscale equations for microchannel fluid flow and heat transfer have been given.

In several cases, operation of microreactors has shown that their expected efficiency can not be reached due to either a non-uniform distribution of reactants between different channels, or due to a flow maldistribution between individual microreactors working in parallel. The latter can result in substantial temperature deviations between different microreactors resulting in thermal runaway which could arise from an exothermic reaction. Thus advances in the understanding of heat transfer and fluid flow distribution continue to be crucial in achieving improved performance, efficiency and safety in microstructured reactors applied for different applications. The experimental and numerical results on fluid flow distribution, heat transfer and combination thereof will be presented. Heat transfer in microchannels can be suitably described by standard theory and correlations, but scaling effects (entrance effects, conjugate heat transfer, viscous heating, temperature dependent properties) have often to be accounted for in microsystems. Experiments with single channels are generally in good agreement with predictions from published correlations. The accuracy of multichannel experiments is lower due to flow maldistribution. A set of design recommendations for purposes of improving reactor performance will be provided.

OP-I-11

ELUCIDATION OF THE REACTIVITY OF DIFFERENT OXYGEN SPECIES OVER V-Ti-O SURFACE TOWARDS PARTIAL OXIDATION OF LIGHT HYDROCARBON USING ISOTOPE METHODS

Sadovskaya E.M.[a], Goncharov V.B.[a], Gulyaeva Yu.K.[a], Andrushkevich T.V.[a], Bal'zhinimaev B.S.[a], Suprun W.[b], Papp H.[b]

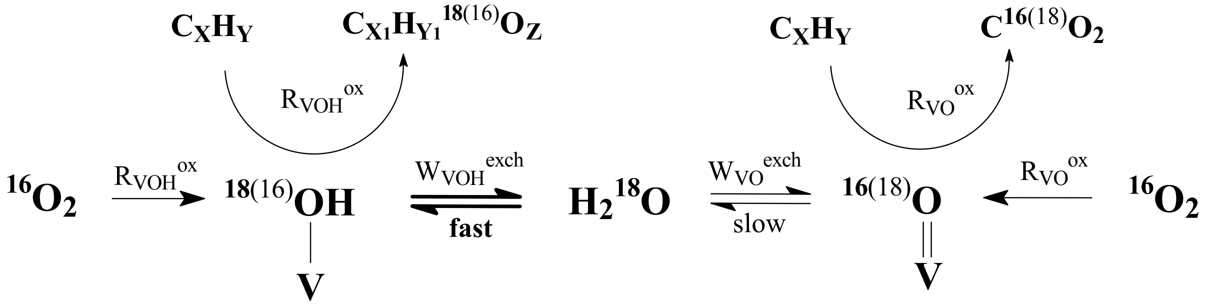
[a]Boreskov Institute of Catalysis SB RAS, pr. Akad. Lavrentieva, 5,
630090, Novosibirsk, Russia, e-mail: sadovsk@catalysis.ru
[b]Institut für Technische Chemie, Universität Leipzig, D-04103 Leipzig, Germany

Vanadia is one of the most efficient catalysts for partial oxidation of hydrocarbons. Despite the fact that mechanism and kinetics of these reactions were intensively investigated over last decades, understanding of the factors influencing reaction pathways and selectivity is still open. Meanwhile, the role of different surface oxygen species in the partial or complete oxidation is intensively discussed, mainly focusing on hydrated V-OH sites [1].

In this study we used the original isotope kinetic approach that allows in situ identification of hydrated and dehydrated sites participating in the reaction. According this method, the isotope composition of oxidation products was determined, while the non-equilibrated distribution of ^{16}O and ^{18}O in VOH and VO was maintained because of difference in the rates of their isotope exchange with $H_2{}^{18}O$ added to the reaction mixture.

Study of the kinetics of isotope exchange of V_2O_5/TiO_2 and $H_2{}^{18}O$ [2] showed that in the temperature range that is typical for the most reactions of partial oxidation (150-250°C) the rate of oxygen exchange of H_2O with VOH groups is more than two orders of magnitude higher than that with VO. So, at 200°C $k_{VOH}^{exch} \approx 0.5\ ^{1}$, $k_{VO}^{exch} \approx 2*10^{-3}$ s^{-1}; $E_{VOH}^{exch} \approx 0$, and $E_{VO}^{exch} = 70$ kJ/mole.

Two competitive processes, i.e. isotope exchange with water resulting in the enrichment of active sites by ^{18}O, and catalyst reoxidation by ^{16}O take place during oxidation of hydrocarbons in the presence of $H_2{}^{18}O$:



^{18}O isotope fractions in VOH and VO (α_{VOH}^{18} and α_{VO}^{18}, respectively) are determined by the ratio between the rate of oxygen exchange $W_{VOH(VO)}^{exch}$ and that of reaction over these sites $R_{VOH(VO)}^{ox}$:

$$\alpha_{VOH(VO)}^{18} = \frac{W_{VOH(VO)}^{exch}\alpha_{H_2O}^{18} + R_{VOH(VO)}^{ox}\alpha_{O_2}^{18}}{W_{VOH(VO)}^{exch} + R_{VOH(VO)}^{ox}}$$

Provided the value of summarized rate of reaction lies between W_{VOH}^{exch} and W_{VO}^{exch}, then α_{VOH}^{18} and α_{VO}^{18} will be substantially different: $\alpha_{VOH}^{18} >> \alpha_{VO}^{18}$. In this case isotope composition of oxidation products depends on the type of active sites participating in their formation.

As an example, the results obtained for partial oxidation of 1-butene to acetic acid (AcOH) have been presented. $H_2{}^{18}O$ addition into the reaction mixture resulted in the transfer of labeled oxygen to AcOH [3]. Numerical analysis of the dynamics of isotope transfer and distribution of differently labeled AcOH molecules ($CH_3{}^{16}O^{16}OH$, $CH_3{}^{16}O^{18}OH$ and $CH_3{}^{18}O^{18}OH$) showed that the hydrated centers exhibit high activity in partial oxidation of 1-butene in contrast to dehydrated VO centers which favor total oxidation. So, the turnover frequency of 1-butene to AcOH over VOH centers is at list three times higher than over VO centers.

References:

[1]. B.S. Balzhinimaev, L.G. Pinaeva, Kinet. Katal. 36 (1995) 50-60.

[2]. E.M. Sadovskaya, V.M. Concharov, Yu.K. Gulyaeva, G.Ya. Popova, T.V. Andrushkevich, J. Molec. Catal. A: Chem. 316 (2010) 118-125.

[3]. W.Y. Suprun, D.P. Sabde, H.-K. Schädlich, B. Kubias, H. Papp, Appl. Catal. A. General 289 (2006) 66-73

KINETIC MODELLING OF THE JOINT TRANSFORMATION OF N-BUTANE AND METHANOL

Mier D.[1], Aguayo A.[1], Gamero M.[1], Bilbao J.[1], Gayubo A.[1]

[1]*Dept. Chemical Engineering, University of the Basque Country, P.O.Box 644. 48080 Bilbao, Spain. E-mail: diana.mier@ehu.es*

The joint transformation of paraffins and methanol [1] for C_2-C_4 olefin production ofers interesting synergies respecto to the two individual processes: i) it is energetically neutral; ii) the olefin yield is increased; iii) and the atenuation by coke is attenuated [2,3].

A kinetic model of lumps has been established for the joint transformation in the 400-550 °C range, based on the results obtained in a fixed bed reactor (space time, up to 9.5 (g of catalyst) h (mol $CH_2)^{-1}$; methanol/n-butane molar ratio in the feed, 3/1 (which corresponds to an energy-neutral process); time on stream, 5 h) over HZSM-5 zeolite catalyst (SiO_2/Al_2O_3 = 30) which is prepared agglomerating 35 wt% of active phase (by wet extrusion) with bentonite as a binder (30 wt%) and inert alumina as charge (45 wt%).

Different kinetic models have been proposed. The discrimination of models and the calculation of kinetic parameters have been carried out by fitting the experimental values of the evolution of each component composition with space time to the calculated values, by solving the corresponding mass conservation equations by using a numerical procedure written in MATLAB.

The kinetic scheme of best fit integrates the stages of individual reactions: cracking of n-butane [4] and MTO process [5] at high temperature and considers the synergies between the stages of both reactions. Moreover, the model allows to quantify the distribution of the lumps of products (Methanol (M), Dimethyl Ether (D), C_2-C_4 olefins (O), C_2-C_4 paraffins (P), n-butane (B), methane (C) and C_5-C_{10} components (G)) in a wide range of temperatures, partial pressures of hydrocarbons in the reaction medium and space time.

Figure 1 shows the diferent stages of the proposed kinetic scheme which takes into account the following steps: i) The dehydration of methanol into dimethy ether and water (k_1); ii) The transformation of methanol and dymethil ether into olefins and methane (k_2-k_5); iii) The transformation of n-butane into light olefins and methane (k_4 and k_6); iv) Five autocatalytic steps by reaction of oxigenates, n-butane, paraffins and

C_5-C_{10} fraction with olefins (intermediates in the general kinetic scheme of reaction) (k_7-k_{11});. v) The formation of final products n-butane, paraffins and C_5-C_{10} fraction (k_{12}-k_{14}).

The kinetic model steps for the transformation of olefins into paraffins, n-butane and C_5-C_{10} are second order with respect to the reactant, whereas the remaining steps are of first order with respect to each reactant.

The godness of fit is shown in Figure 2 where the experimental resuts (points) of lump composition are comparated with those calculated using the kinetic model (lines).

When the target is the production of C_2-C_4 olefins, the yield is limited to 20 %, at 550 °C and methanol/n-butane molar ratio = 3/1.

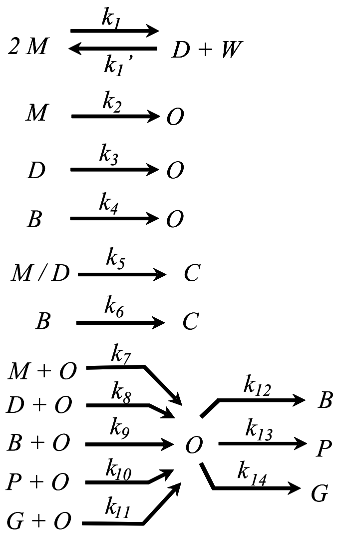


Figure 1: Kinetic scheme proposed for the combined n-butane and methanol cracking.

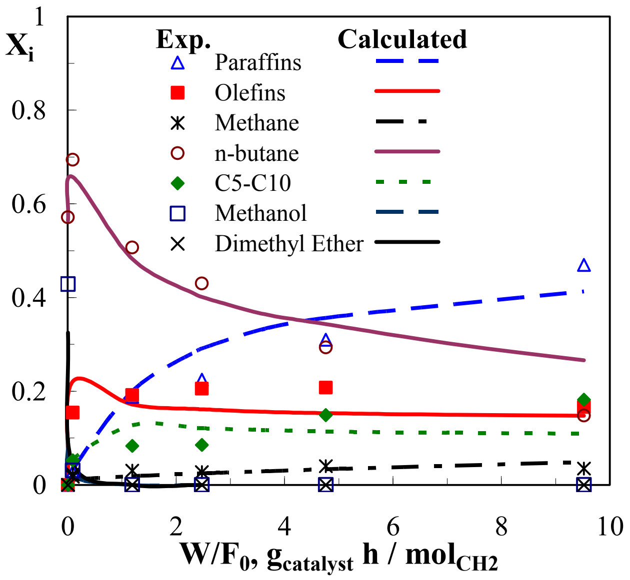


Figure 2: Comparison of the evolution with space time of the experimental values (point) and those calculated (lines) with the kinetic model at 550 °C.

References

[1]. Martin, A.; Nowak, S.; Lücke, B.; Wieker, W.; Fahlke, B. *Appl. Catal.* **1990**, *57*, 203-214.

[2]. Mier, D.; Aguayo, A.T.; Atutxa, A.; Gayubo, A.; Bilbao, J. *Int. J. Chem. React. Eng*. **2007**, *5*, A60.

[3]. Mier, D.; Aguayo, A.T.; Gayubo, A.; Olazar, M.; Bilbao, J. *Appl. Catal. A: Gen.* **2010**, in press.

[4]. Guisnet, M.; Gnep, N. S.; Aittaleb, D.; Doyement, Y. J. *Appl. Catal. A: Gen.l* **1992**, *87*, 255-270.

[5]. Gayubo, A. G.; Aguayo, A. T.; Castilla, M.; Olazar, M.; Bilbao, J. *AIChE J*. **2002**, *48*, 1561-1571.

n-HEXANE SKELETAL ISOMERIZATION OVER BYFUNCTIONAL CATALYSTS: EXPERIMENT AND KINETIC MODELING

Volkova G.G., Budneva A.A., Paukshtis E.A., Petrov R.V., Reshetnikov S.I.

Boreskov Institute of Catalysis SB RAS, Pr. Akademika Lavrentieva 5,
Novosibirsk, 630090, Russia, E-mail: ggvolkova@catalysis.ru

Skeletal isomerization of light naphtha is composed mainly of conversion of *n*-hydrocarbons C_5-C_8 into branched alkanes. It allows to increase octane number of gasoline because multiply branched alkanes have higher octane number than mono-methyl alkanes, and are preferentially produced at low temperature subject to chemical equilibrium. By the large demand of desired isomerization products development of new more active catalysts has been continued. Recently new acid catalysts based on sulfated zirconia have been developed and successfully commercialized [1–2]. It is known that activity of the sulfated zirconia catalysts significantly depends on preparation procedure, the activity of the catalysts with the same structure and equal in sulfate content may differ by one order of magnitude. Many researchers try to reveal the critical differences determining the variation in catalytic activity and to recognize the important characteristics of the active catalyst.

The aim of this work was to investigate the kinetics of *n*-hexane skeletal isomerisation over bifunctional catalysts with different acidity: $Pt/Cs_2HPW_{12}O_{40}$ $Pt/WO_x/ZrO_2$; $Pt/SO_4/ZrO_2$.

The calculation of the rate constants, characterizing the catalyst activity and selectivity was performed on the base of mathematical model of plug flow reactor. It was assumed that the reactions are pseudo-first order in reagents. It was shown that the rate of hexane isomerization is mainly determined by the density of Lewis acid sites on the surface of catalysts The kinetic constants and activation energies were determined. The results of mathematical modeling are in good agreement with experimental data.

References

[1]. T. Kimura, Catal. Today **2003,** *81*, 57.
[2]. S.A. Gembicki, Stud. Surf. Sci. Catal. **2000**, *130*, 147.
[3]. X. Li, K. Nagaoka, L.J. Simon, J.A. Lercher, S. Wrabetz, F.C. Jentoft, C.Breitkopf, S. Matysik, H. Paap, J.Catal. **2005**, *230*, 214.

Acknowledgements

This work is supported by Federal Target Program (FTP) ”Science, Academic and Teaching Staff of Innovative Russia for 2009-2013”. Contract P253.

THE EXPERIENCE OF KINETIC MODEL DESIGN FOR CYCLOHEXENE CATALYTIC OXIDATION BY p-QUINONES IN THE CATIONIC PALLADIUM (II) COMPLEXES SOLUTIONS. A NEW WAY TO CYCLOHEXANONE

Temkin O.N., **Katsman E.A.**, **Bruk L.G.**, **Zakharova D.S.**

Moscow State Academy of Fine Chemical Technology, Vernadsky Pr. 86,
Moscow, 119571, Russia, e-mail: olegtemkin@mail.ru

p-Quinones (Q) play an important role in electron and proton transfer in oxidative transformations in biochemical reactions and in chemical oxidative catalysis with metal complexes. They act a) as oxidants of the metal catalysts reduced forms, b) as oxidants and catalysts of the intermediates demetallization steps and c) as ligands for the active catalyst forms stabilization [1,2]. It is known that cationic Pd(II) complexes in water and water-organic solvents are very active catalysts of α-olefines and cycloolefines oxidation to ketones by p-quinones [3-6]. After the new technology designed by Asahi Com. for the cyclohexene (CH) production from benzene the new process of the cyclohexanone synthesis by CH oxidation by Q and oxygen comes into particular interest. The unexpected kinetic behaviour of the system: $Pd(OAc)_2$ – $HClO_4$ – Q –CH_3CN – H_2O [7,8] makes this reactions an interesting object for mechanistic studies and kinetic model design too. The results of kinetic study of CH oxidation in this system are presented In this report.

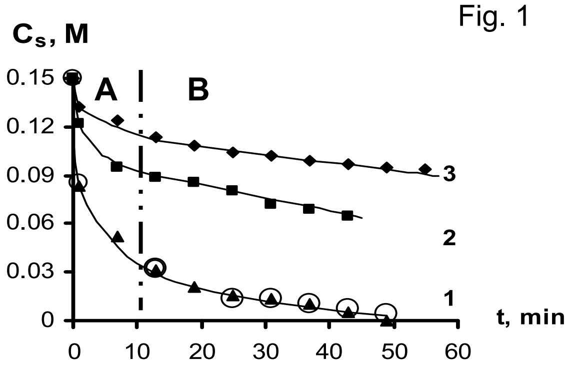


Fig. 1

The preliminary investigations showed [7] the existence of two parts on kinetic curves (Fig. 1) – fast (**A**) and slow (**B**). The initial reaction rates increase up to maximum with $[HClO_4]_0$ and $[Q]_0$ growth, depend on the Q nature and increase with Pd concentration according to the S-type curve. The kinetic data are not described by the known kinetic model of one route reaction of the Wacker-process in the quasi-steady-state conditions [9]. The TEM experiments showed the absence of the colloids and nanoclusters with the size more then 1 nm.

To explain the presence of **A** and **B** parts on the kinetic curves, the weak dependence of the reaction rates on the substrate and palladium concentrations on

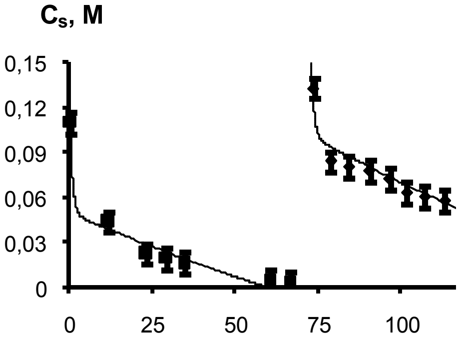


Fig. 2

the slow branch of kinetic curves (Fig. 1) and the repetition of the curves after the addition of substrate at the end of reaction (Fig. 2) the discrimination of the mechanistic hypotheses with a number of routes 2-5 was carried out.

The key features of these hypotheses were the rapid reduction of initial $Pd(CH_3CN)_x(H_2O)_y^{2+}$ complexes by CH into Pd_2Q^{2+} and PdQ^0 complexes, which are true active catalysts. The reaction scheme based on these suggestions with the best description of experimental data includes 5-route mechanism (Fig. 3) with the additional step

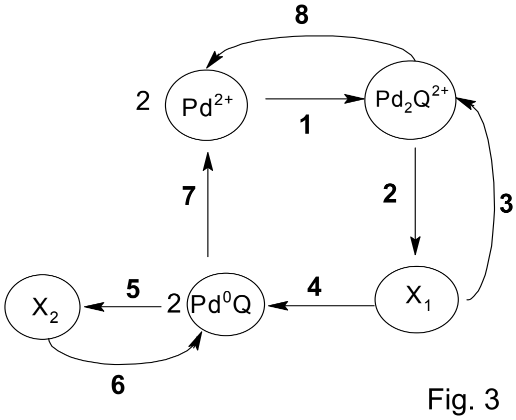
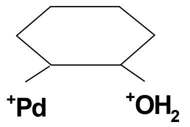


Fig. 3

$$PdQ^0 + Pd^{2+} \overset{(9)}{\rightleftharpoons} Pd_2Q^{2+}$$

.

The ways of transformations of the primary intermediate - metalcarbenium ions solvated by water molecule and the mechanisms of oxidative catalysis with these particles are discussed. Non-Wacker reaction mechanisms is in line with the fact that the reaction rates ratio of C_3H_6 and C_2H_4 oxidations is near 40 in the acidic water solution of Pd^{2+} [4].



Authors thank RFBR for financial support, grant № 307-03-00315 and № 10-03-00326.

References

[1]. Temkin O.N., Bruk L.G., Kinet. i Kataliz, 2003,.**44**, № 5, p. 601.

[2]. Temkin O.N., Homogeneous Catalysis with Metal Complexes. Kinetic Aspects. M., Academkniga, 2008, 918 p.

[3]. Matveev K.I., Shitova N.B., Zhizhina E.G., Kinet. i Kataliz, 1976, **17**, № 4, p.893.

[4]. Zhizhina E.G., Shitova N.B., Matveev K.I., Kinet. i Kataliz, 1981, **22**, № 6, p.1451.

[5]. Backvall J.-E., Hopkins R.B., Tetrahedron Lett., 1988, **29**, Iss.23, p. 2885.

[6]. MillerD.G., Wayner D.D.M., J. Org. Chem., 1990, **55**, p.2924.

[7]. Temkin O.N., Bruk L.G., Petrov I.V., Zakharova D.S., Book of Abstracts, ISHC-XVI, Florence, Italy, 2008. p.P021.

[8]. Temkin O.N. Bruk L.G., Zakharova D.S., Odintsov K.Yu., Katsman E.A., Petrov I.V., Istomina O.Yu., Kinet. i Kataliz, 2010 (in print).

[9]. Moiseev I.I., Levanda O.G., Vargaftik M.N. // J. Am. Chem. Soc., 1974, **96**, Iss.4, p.1003.

OP-I-15

MECHANISM OF THE COUPLED CO OXIDATION AND CYCLOHEXENE HYDROCARBOXYLATION IN THE SYSTEM $PdBr_2$-$CuBr_2$-H_2O-TETRAHYDROFURAN

Bruk L.G., Bukina E.Yu., Demidova S.V., Trunilina K.V., Kirichek I.D., Oshanina I.V., Temkin O.N., Shvats A.L.

Moscow state academy of fine chemical technology,
Vernadsky Pr. 86, Moscow, 119571, Russia, E-mail: lgbruk@mail.ru

Coupled (or conjugate) reactions have common intermediates and mutual effect each to another (chemical induction)[1]. The first theory of coupled reactions was developed by V. Ostvald and N.A. Shilov and was used to describe of phenomenology of such processes. Modern kinetic theory for multyroute reactions allows us to describe chemical coupling phenomenon in all particular cases: thermodynamic and kinetic conjugation, kinetic conjugation only, chemical induction. It was shown by Boudart, that thermodynamic conjugation (together with kinetic one) may be realized only for consecutive steps, having common intermediate [3]. Classification was proposed for conjugated reactions. One includes one-route, two-route and multyroute mechanisms with different kinds of coupling [4]. This approach allowed us to propose principle of kinetic conjugation of reactions (PKCR). PKCR means creation coupled process using information about probable mechanisms of reactions to be coupled. Conjugate process creation can decrease thermodynamic and (or) kinetic difficulties to transform reagents to aimed products. One of the applications of PKCR is to increase capacity of catalyst design [4-6].

Reaction (1) is often used as basic one to produce intermediate (or catalyst) responsible for coupling and to organize conjugate process, for example (2) [7].

$$CO + 0.5\ O_2 = CO_2 \tag{1}$$

$$CO + H_2O + O_2 \overset{Pd(OAc)_2\text{-}PPh_3\text{-}CH_2Cl_2}{=} CO_2 + H_2O_2 \tag{2}$$

It was shown that reaction (2) is carried out in the catalytic system $PdBr_2$-$CuBr_2$-S (S – 1,4-dioxane, tetrahydrofuran) too [4]. Adding of alkene into this system leads to reaction (3). Cyclohexane acid is the only product of (3) in the case of cyclohexene (4). New coupled process is carried out under mild conditions (30°, 0.1 MPa of mixture $CO+O_2$).

$$RCH{=}CH_2 + CO + H_2O \rightarrow RCH_2CH_2COOH + RCH(COOH)CH_3 \tag{3}$$

$$C_6H_{10} + CO + H_2O = C_6H_{11}COOH \tag{4}$$

The hydride palladium complexes are the most probable intermediates to be responsible for coupling of reactions (1) and (3) or (4)[4,5]. These complexes may be received by oxidation carbon monoxide with palladium(II) (5) and ones are well studied catalysts for alkene hydrocarboxylation to saturated acids [8].

This report deals with results of mechanistic study of conjugate process (1)+(4). Hypothetical mechanisms were discriminated using results of kinetic (including kinetic isotop effect of changing H_2O by D_2O) and of nonkinetic (UV- and VIS-, IR-spectroscopy of model and reaction solutions) studies. As result: the most probable mechanism includes hydride palladium complex formation in steps 5, 6 (oxidation of CO). This complex catalyzes cyclohexene hydrocarboxylation (steps 7-10) and is oxidized by oxygen to hydrogen peroxide (steps 12,13).

$$PdX_2(CO)_2 + H_2O \leftrightarrow PdX_2(CO)(COOH_2) \quad (5)$$

$$PdX_2(CO)(COOH_2) + CO \rightarrow HPdX(CO)_2 + CO_2 + HX \quad (6)$$

$$HPdX(CO)_2 + C_6H_{10} \leftrightarrow HPdX(CO)(C_6H_{10}) + CO \quad (7)$$

$$HPdX(CO)(C_6H_{10}) \rightarrow XPd(CO)(C_6H_{11}) \quad (8)$$

$$XPd(CO)(C_6H_{11}) + CO \rightarrow XPdC(O)(C_6H_{11})(CO) \quad (9)$$

$$XPdC(O)(C_6H_{11})(CO) + H_2O \rightarrow HPdX(CO) + C_6H_{11}COOH \quad (10)$$

$$HPdX(CO) + CO \leftrightarrow HPdX(CO)_2 \quad (11)$$

$$HPdX(CO) + O_2 + CO \rightarrow (CO)_2XPdOOH \quad (12)$$

$$(CO)_2XPdOOH + HX \rightarrow PdX_2(CO)_2 + H_2O_2 \quad (13)$$

$$HPdX(CO) + C_6H_{10} \leftrightarrow HPdX(CO)(C_6H_{10}) \quad (14)$$

$$2H_2O_2 \rightarrow 2H_2O + O_2 \quad (15)$$

Chemical conjugation and chemical induction take place in this mechanism being in accordance with all experimental data.

Referenses

[1]. Khimicheskaya entsiklopediya (Chemical encyclopaedia)// M.: Bolshaya rossiyskaya entsiklopediya, 1995, V.4, 767 p.

[2]. Shilov N.A. O sopryajennikh reaktsiyakh okisleniya// M., 1905, 304 p.

[3]. Boudart M.// *J. Phys. Chem.* 1983, V. 87, P. 2786.

[4]. Bruk L.G., Abdullaeva A.S., Temkin O.N. et al.// In Abstracts 14-th Int. Symp. Homog. Catal., Munich, 2004, PO124.

[5]. Bruk L.G., Oshanina I.V., Temkin O.N. et al.// *Ros. Chim. J.* 2006, V. L, 4, P. 103.

[6]. Bruk L.G.,Abdullaeva A.S., Timashova E.A. et al. *Kinetika i Kataliz*, 2010, in press.

[7]. Likholobov V.A., Ermakov Yu.I. *Kinetika i Kataliz,* 1980, V. 21, P. 904.

Financial support of RFBR, grant 08-03-00258.

OP-I-16

DEVELOPMENT OF A CFD BASED PROCESS SIMULATION CAPABILITY FOR A FISCHER-TROPSCH REACTOR

Antal S.P.[1], **Jordi R.**[2], **Combes G.**[3]

[1]*Interphase Dynamics, Ballston Lake, USA, antals@rpi.edu*
[2]*Sasol Technology, Sasolburg, South Africa*
[3]*Johnson Matthey PLC, Middlesbrough, UK*

This paper presents a computational multiphase fluid dynamics (CMFD) model of a Gas-To-Liquid (GTL) reactor utilizing the Fischer-Tropsch conversion process. The goal of the CMFD model is to accurately predict both the hydrodynamic flow profiles and the local reaction kinetic rate. A typical pilot sized (1m diameter) Fischer-Tropsch (FT) process reactor demonstrates the capability of the model to better understand the hydraulic and reaction engineering. Previous work, References [1] and [2], have shown the hydraulic model capable to accurately simulate two-phase flow profiles in a bubble column and churn-turbulent flows. To validate the reaction chemistry in the CMFD computer code, a one dimensional model is compared to well accepted hand calculations to verify the implementation and test its accuracy.

The GTL reactor is assumed to operate in either the bubbly, churn-turbulent, or mixed bubbly-churn flow regime. In each of these operating conditions the gas-liquid interface forces, which control the gas holdup and liquid flow profiles, can be very different. To accurately capture the flow physics a five field model of two-phase flow was implemented with the NPHASE-CMFD [3] computer code. The five fields chosen include the liquid “l”, very small bubbles “vsb” (diameter < 1 mm), small bubbles “sb” (diameter 1 to 10 mm), large cap/slug bubbles “lb” (diameter > 10mm), and the catalyst particles “p”. The use of separate fields allow different closure model physics to describe the interfacial forces on each field. The ensemble averaged [4] conservation equations, used as the framework for this technology, can be written as:

Mass Conservation (field j)

$$\frac{\partial}{\partial t}\left(\alpha_j \rho_j\right) + \nabla \cdot \left(\alpha_j \rho_j \underline{u}_j\right) = m_j'''$$

Momentum Conservation (field j)

$$\frac{\partial}{\partial t}\left(\alpha_j \rho_j \underline{u}_j\right) + \nabla \cdot \left(\alpha_j \rho_j \underline{u}_j \underline{u}_j\right) = -\alpha_j \nabla p_j + \nabla \cdot \alpha_j \left(\underline{\underline{\tau}}_j + \underline{\underline{\tau}}_j^{\mathrm{Re}}\right) + \alpha_j \rho_j g + \underline{M}_j + m_j''' \underline{u}_i$$

Energy Conservation (field j)

$$\frac{\partial}{\partial t}\left(\rho_j h_j\right)+\nabla\cdot\left(\rho_j \underline{u}_j h\right)=\nabla\cdot\left(q_j^{''}+q_j^{''T}\right)+\Delta H_i+h_c A(T_j-T_{surface})$$

The FT synthesis reaction kinetics process is modeled using a macrokinetic rate experssion developed by Yates and Satterfield, References [5] and [6]. A simplified reaction equation is used in this capability demonstration as:

$$\mathrm{CO}+2\mathrm{H}_2\rightarrow\mathrm{CH}_2+\mathrm{H}_2\mathrm{O}$$

To account for the local reaction rates, both reactants (CO and H_2) and both products (CH_2 and H_2O) will be tracked in the liquid solvent, very small bubbles, small bubbles and large cap/slug bubbles. Therefore, 16 separate species mass fractions (Y_i) will be tracked throughout the reactor using a species transport equation as:

Species Mass Fraction Transport (species s in carrier field j)

$$\frac{\partial}{\partial \mathrm{t}}\left(\alpha_{\mathrm{j}}\rho_{\mathrm{j}}\mathrm{Y}_{\mathrm{s}}\right)+\nabla\cdot\left(\alpha_{\mathrm{j}}\rho_{\mathrm{j}}\underline{\mathrm{v}}_{\mathrm{j}}\mathrm{Y}_{\mathrm{s}}\right)=\nabla\cdot\alpha_{\mathrm{j}}\left(\frac{\mu_{\mathrm{j}}}{\sigma_{\mathrm{s}}}+\frac{\mu_{\mathrm{j}}^{\mathrm{T}}}{\sigma_{\mathrm{s}}^{\mathrm{T}}}\right)\nabla\mathrm{Y}_{\mathrm{s}}+\mathrm{S}_{\mathrm{s}}$$

The paper will include both hydraulic and reaction kinetic profiles in a typical pilot size demonstration FT reactor. Novel modeling will be presented to include the flashing of water in the liquid solvent to steam in the gas phase. Finally, the predicted temperature profiles and liquid fuels production rates will be presented. In addition, lessons learned in applying advanced technology to the reaction process industry and future work will be summarized.

References

[1]. Antal, S.P., R.T. Lahey, Jr., M.H. Al-Dahhan, Simulating Churn-Turbulent Flows in a Bubble Column using a Three-Field, Two-Fluid Model, in 5th International Conference on Multiphase Flow, ICMF'04. 2004: Yokohama, Japan.

[2]. Tselishcheva, E.A., et.al., “Development and Validation of a Multifield Model of Churn-Turbulent Gas/Liquid Flows,” Proceedings of the 17th International Conference on Nuclear Engineering, ICONE17, July 12-16, 2009, Brussels, Belgium.

[3]. Drew, D.A., Passman, S.L. "Theory of Multicomponent Fluids", Applied Mathematical Sciences, Vol. 135, (1998)

[4]. [Antal, S.P., Kunz, R., Ettore, S., Podowski, M.Z., 2000. Development of a next generation computer code for the prediction of multicomponent multiphase flows. In: Proceedings of the International Meeting on Trends in Numerical and Physical Modeling for Industrial Multiphase Flows, Cargese, France.

[5]. Yates, I.C. and Satterfield, C.N., "Intrinsic Kinetics of the Fischer-Tropsch Synthesis on a Cobalt Catalyst", Energy & Fuels, **5**: p. 168-173, (1991)

[6]. Guillen, D.P., et.al. , “Incorporation of Reaction Kinetics into a Multiphase, Hydrodynamic Model of a Fischer Tropsch Slurry Bubble Column Reactor”, AIChE Annual Meeting, Philadelphia, PA, Nov. 2008.

OP-I-17

KINETICS PARTICULARITIES OF PHENOL HYDROGENATION OVER Pd IMPREGNATED HYPERCROSSLINKED POLYSTYRENE

Sulman E.[1], **Chernyavsky V.**[2], **Ivanov A.**[2], **Sulman M.**[1],
Matveeva V.[1], **Kharitonov A.**[2]

[1]*Tver State Technical University, Institute of Nano and Biotechnologies, Tver,*
Nab. A. Nikitina 22, sulamn@online.tver.ru
[2]*Boreskov Institute of Catalysis, Novosibirsk, Russia, khar@catalysis.ru*

Phenol hydrogenation over Pd based catalysts is widely used in industry for cyclohexanone synthesis in caprolactam production. The main reaction products are cyclohexanone and cyclohexanol. Process engineers try to obtain the maximal phenol selectivity for cyclohexanone at full phenol conversion. The use of Pd hypercrosslinked polystyrene catalyst can be an essential step toward this goal.

In the literature, phenol hydrogenation is considered as a two-route reaction with successive conversion of phenol to cyclohexanone according to the scheme:

1) $C_6H_5OH + 2H_2 = C_6H_{10}O$
2) $C_6H_{10}O + H_2 = C_6H_{11}OH$

The reaction is assumed to proceed by the Langmuir–Hinshelwood mechanism. To refine the route scheme for a new catalyst, we studied the kinetic regularities under wide variation of phenol conversion in a steel isothermal flow reactor over the temperature range of 120 to 181°C. The inlet concentrations were 11% for phenol and 80% for hydrogen. The 0.5 g catalyst sample was diluted with quartz grains in the ratio of 1 to 3. The bed height was 23 cm. The catalyst was prepared by impregnating the spherical particles of hypercrosslinked polystyrene with a solution of Na_2PdCl_4. The content of palladium in the catalyst was 0.5 wt %. Active metal nanoparticles were mainly distributed nearby the outside surface of polymer granules, the thickness of saturated layer was found to be 0.04 mm. The catalyst was characterized by XPS, XFA, nitrogen physosorption, transmition electron microscopy and FTIR CO. Figure 1 shows selectivity for cyclohexanone versus phenol conversion at different temperatures. The dependences indicate that the minimum number of routes is three. Along with the above mentioned routes, there is an additional route of cyclohexanol formation:

3) $C_6H_5OH + 3H_2 = C_6H_{11}OH$

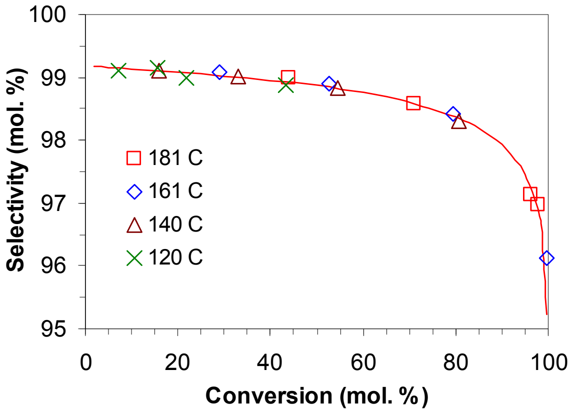


Fig. 1. Phenol selectivity for cyclohexanone vs phenol conversion. Line is the result of calculations (Eq. 2). Points are the experimental data.

Supposing all the routes proceed at the same sites, expressions for the route rates will be identical at a high excess of hydrogen. A set of equations for cyclohexanone and cyclohexanol formation rates will look as

$$\frac{dx}{d\tau} = k_{\Sigma}(1-x)\cdot f(c)$$

$$\frac{dy}{d\tau} = k_1(1-x)\cdot f(c) - k_2 y\cdot f(c) \qquad (1)$$

where x is the phenol conversion, y is the yield of cyclohexanone, $k_{\Sigma} = k_1 + k_3$ is the total rate constant of phenol conversion over routes 1 and 3, k_2 is the rate constant over route 2, and f(c) is a function of the reaction components concentrations that determines the stationary concentrations of intermediates on the catalyst surface.

Integration of the set of equations gives

$$s = \frac{s_0}{x(1-b)}\cdot[(1-x)^b - (1-x)] \qquad (2)$$

Selectivity (S) is determined by two parameters, $s_0 = k_1/k_{\Sigma}$ and $b = k_2/k_{\Sigma}$, which depend on the catalyst properties.

As seen from Figure 1, the experimental dependences of selectivity on conversion are satisfactorily described by equation 2. The selectivity is temperature independent (in coordinates x – S), which is an essential feature of this catalyst. Reaction rate is described by the first order equation with respect to phenol. Activation energy for all the routes was 51 kJ/mol. Taking into account kinetic characteristics, a maximum yield that can be attained on this catalyst is 95.3% at phenol conversion 99.2%. A comparison with the known catalytic systems was made.

Acknowledgements

We sincerely thanks Russian agency of science and innovation for financial support (contract numbers 02.740.11.0145; 02.740.11.5104, 02.552.11.7075).

OP-I-18

DEVELOPMENT OF SELECTIVE CAMPHENE SYNTHESIS FROM α-PINENE OVER GOLD ON γ-ALUMINA OXIDE

Simakova I.L.[1], Solkina Yu.S.[1,2], Moroz B.L.[1,2], Simakova O.A.[1,3], Reshetnikov S.I.[1], Simakov A.V.[4], Murzin D.Yu.[3], Parmon V.N.[1,2]

[1]Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia,
simakova@catalysis.ru
[2]Novosibirsk State University, Novosibirsk, Russia
[3]Åbo Akademi University, Process Chemistry Center, Turku/Åbo, Finland
[4]Centro de Nanociencias y Nanotecnologia UNAM, Ensenada, B.C., Mexico

The sustainable production of fine chemicals from biomass and renewable feedstocks are recently under growing interest. Wood turpentine isolated by the distillation of resin obtained from trees, mainly pine trees, or collected as a byproduct when producing chemical wood pulp from pines or other coniferous trees with the Kraft process, is inexpensive starting material for synthesis of chemicals. The main components in turpentine oil - α-pinene, β-pinene and 3-carene - are key ingredients in the flavour and fragrance industry [1]. Earlier it was reported that α-pinene can be transformed over Pd/C catalysts into *cis*- and *trans*-pinanes [2,3], linalool and geraniol [4,5]. Bulk gold is in general regarded poorly active as a heterogeneous catalyst, but when gold is deposited on a proper metal oxides as ultra-fine particles its chemistry changes [6]. In the present work we developed the original method of selective camphene synthesis from α-pinene over gold deposited on γ-alumina.

The isomerization of α-pinene to camphene was carried out in a fixed bed glass reactor over 2.2 wt. % Au/γ-Al_2O_3 at temperature 463-483K and atmospheric hydrogen pressure using *n*-octane as a solvent. Catalyst 2.2 wt. % Au/γ-Al_2O_3 was prepared by impregnation of γ-Al_2O_3 (S_{BET}=268 $m^2 \cdot g^{-1}$, pore volume =0.69 $cm^3 \cdot g^{-1}$) with $HAuCl_4$ (49.47 wt % Au, Aurat, Russia) aqua solution as described in [7]. Gold catalysts (fresh and spent) were characterized by TEM, XPS, XRF, UV–VIS and TPO.

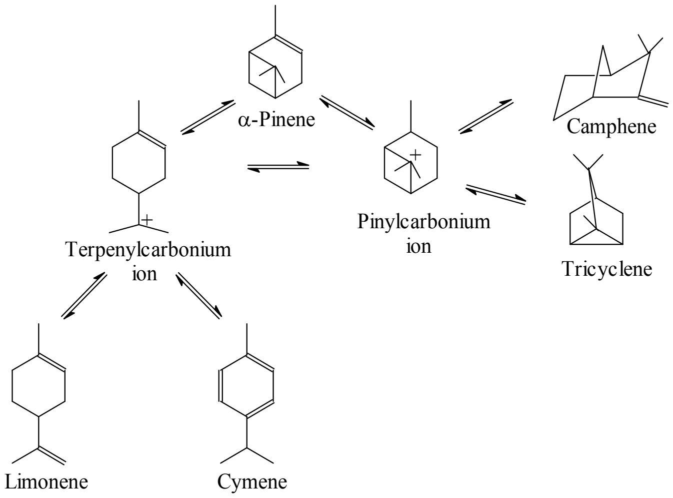


Figure 1. The scheme of α-pinene isomerization

According to GLC the main products are camphene, limonene, p-cymene and tricyclene (Fig. 1). The selectivity towards camphene (60-80 %) and α-pinene conversion (99.9 %) over Au/γ-Al_2O_3 catalyst were exceptionally high.

The general kinetic regularities of the vapour-phase α-pinene isomerization over Au/γ-Al_2O_3 catalyst were established. The effect of temperature (Fig. 2), residence time and initial α-pinene concentration on the α-pinene conversion and the camphene selectivity was studied. The catalyst deactivation during reaction was studied by TEM, temperature-programmed oxidation (TPO) and FT-IR spectroscopy. It was found that predominant coke formation and insignificant amount of oligomers on the catalyst surface causes the catalyst deactivation. It was shown that the catalyst activity can be regenerated completely by the oxygen treatment directly in the same reactor where the process occurs (Fig. 3).

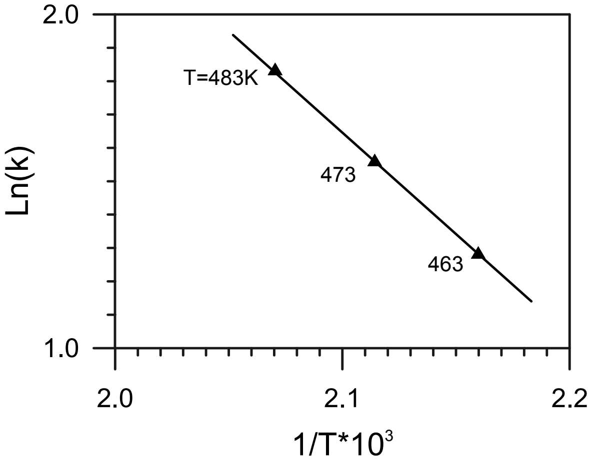


Figure 2. The Arrhenius plot of the rate constant. The reaction conditions: T=463-483 K, α-pinene concentration 20.0 vol. %, residence time 0.05-0.45 s.

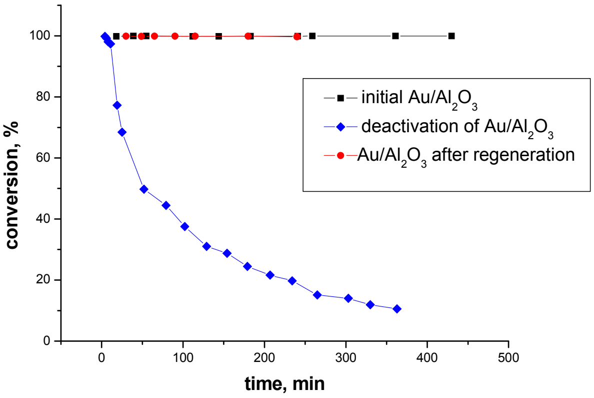


Figure 3. Catalyst regeneration. Reaction conditions: residence time 0.33 s, T=473 K, α-pinene concentration 0.4 vol.% (●,■) and 4.0 vol. % (♦).

To conclude the original method of selective camphene synthesis from renewable α-pinene over 2.2 wt. % Au/γ-Al_2O_3 was developed.

References

[1]. K.A.D. Swift, Topics Catal., **2005**, v. 27,p. 143.
[2]. I. Simakova, Yu. Solkina, I. Deliy, J. Wärnå, D. Yu. Murzin, Appl. Catal. A, **2009, v.**356, p. 216.
[3]. I.V. Deliy, I.L. Simakova, Russian Chemical Bulletin, **2008**, v. 57, # 10, p. 2021.
[4]. V.A. Semikolenov, I.I. Ilyna, I.L. Simakova, Appl. Catal. A, **2001**, v. 211, # 1, p. 91.
[5]. I.L. Simakova, V.A. Semikolenov, Chemistry for sustainable development, **2003**, v. 11, # 1, p. 271.
[6]. M. Haruta, Catal. Today, **1997**, v. 36, p. 153.
[7]. B.L. Moroz, P.A. Pyrjaev, V.I. Zaikovskii, V.I. Bukhtiyarov, Catal. Today, **2009**, v. 144, p. 292.

Acknowledgements

The research work was supported by RFBR Grant № 08-03-91758-AF (Russia), RFBR Grant № 10-03-01005-a and partly by UNAM project PUNTA (Mexico) and PAPIIT IN224510.

OP-I-19

3D CFD SIMULATIONS OF THE EFFECT OF CONTACT ANGLE AND NOZZLE PLACEMENT ON GAS-LIQUID FLOW IN SQUARE MINICHANNELS AT LOW CAPILLARY NUMBER

Erkoc E., Bauer T., Lange R.

Dept. of Chemical Engineering, Technische Universität Dresden, Germany
ertugrul.erkoc@tu-dresden.de

Micro/mini-channels offer the advantage of decreased size of the distance that heat and mass is transported. Taylor flow in such channels, which is characterized by elongated gas bubbles and liquid slugs, have been the interest of number of studies because of the advantages it offers, while having decreased distances of transport. The flow is further caharcterized by the vortex formation in the liquid slug that improves the radial mass and heat transport. Transport characteristics of such systems are affected by the hydrodynamic properties of the flow, such as thickness of the liquid film surrounding the bubble, bubble and slug lengths and velocities inside the channel, mixing and flow circulation in the liquid slug, and pressure drop [1]. As the hydrodynamics are determined by the operating variables and design variables as well as physical and thermodynamic properties, many researchers studied the effect of operating variables such as gas and liquid superficial velocities [2], design variables such as nozzle dimensions [3, 4], and as a combined effect of these variables along with the physical properties of the fluids, by analysing the effect of the dimensionless numbers such as Capillary, Reynolds, Weber. In this aspect, all the given correlations of Taylor flow regarding bubble and slug dimensions and liquid film thickness are based on the mentioned parameters above. As these parameters are curiciously important to model heat and mass transfer in all the directions, it is important to understand the effects of all variables affecting on these parameters. One of the important parameters missing in the correlations is the contact angle of the fluid with the surrounding wall. Recently, it has been shown by 3D CFD study that contact angle affects the bubble formation time significantly [5]. In a visualization study of the liquid film thickness by experiments using different working fluids, it was shown that the contact angle affects the liquid film thickness, too [6]. As visualization studies can be performed only for transparent systems, and in case of chemical industry, washcoated untransparent systems are used, thereby changing the property of the surface, there is a need to clarify the contact angle effect on bubble and slug dimensions, formation time and film thickness. This study aims to achieve this purpose and additionaly, it aims to understand the effect of nozzle displacement inside the capillary, as until now only the effect of dimensions of the nozzle was studied. The 3D CFD simulations were performed using VOF technique for low Capillary number of 0.0016 for a 1.0 mm square cross sectioned minichannel using a nozzle of 0.6 o.d. and 0.315 i.d. Various capillary contact angles from 0 to 90 degrees were studied for a centered nozzle and for a selected contact angle, the effect of nozzle displacement were studied by changing the place of the nozzle, and for a specific contact angle, the 3D simulations were validated with the experiments in terms of bubble and slug dimensions and bubble formation time. It is shown that the contact angle has significant effect not only on bubble formation time but also on film thickness, and bubble and slug lengths.

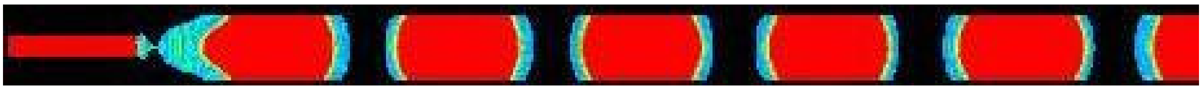


Figure 1 shows a snapshot for two different contact angles and their effets on bubble and slug lengths as well as the film thickness around the gas bubble.

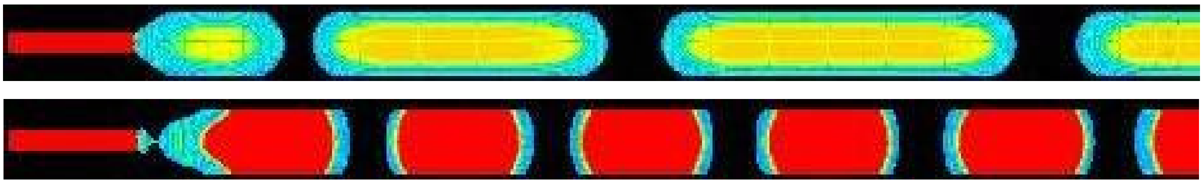


Figure 1. Snapshots of hydrogen and alpha-methylstyrene two-phase flow inside the minichannel for the contact angle of 0 (top) and 60 (bottom) degrees at the capillary number of 0.0016. The direction of flow is from left to the right.

References

[1]. Angeli, P. and A. Gavriilidis, Hydrodynamics of Taylor flow in small channels: a review. Proceedings of the Institution of Mechanical Engineers, Part C: Journal of Mechanical Engineering Science, **2008**. *222(5)*: p. 737-751.

[2]. Mogalicherla, A.K. and D. Kunzru, Effect of Gas and Liquid Superficial Velocities on the Performance of Monolithic Reactors. Industrial & Engineering Chemistry Research **2010**. *49(4)*:p.1631-1641.

[3]. Chen, Y., R. Kulenovic, and R. Mertz, Numerical study on the formation of Taylor bubbles in capillary tubes. International Journal of Thermal Sciences, **2009**. *48(2)*: p. 234-242.

[4]. Shao, N., et al., CFD simulations of the effect of inlet conditions on Taylor flow formation. International Journal of Heat and Fluid Flow, **2008**. *29(6)*: p. 1603-1611.

[5]. Goel, D. and V.V. Buwa, Numerical Simulations of Bubble Formation and Rise in Microchannels. Industrial & Engineering Chemistry Research, **2008**. *48(17)*: p. 8109-8120.

[6]. Han, Y. and N. Shikazono, Measurement of liquid film thickness in micro square channel. International Journal of Multiphase Flow, **2009**. *35(10)*: p. 896-903.

Acknowledgements

The authors are grateful to Deutsche Forschungsgemeinschaft (DFG) for financial support of the research project.

OP-I-20

CFD INVESTIGATION OF MIXING AND SHEAR IN LAB AND PILOT SCALE STIRRED TANK REACTORS DURING HOTWASH

Robin G. Jordi

Sasol Technology Process Development R & D, Sasolburg, South Africa,
robin.jordi@sasol.com

This paper presents computational fluid dynamic models of the hotwash cycle of gas-liquid continuously stirred tank reactors (CSTR) utilised in studies of a homogeneously catalysed oligomerization reaction. This reaction produces deposits of an unwanted polymeric by-product causing fouling of the internal surfaces and requiring the reactor to be operated in campaigns alternating with a hotwash cycle to remove such deposits.

The purpose of the study was to determine and compare shear rates within the CSTR and on polymer surfaces, evaluating the impact of scale to assist in scale-up to commercial scale units, and to predict the distribution of solvent in the pilot scale vessel which was difficult to assess independently.

Extensive piloting in an agitated bubble column was conducted in a pilot scale unit consisted of a baffled 316 litre jacketed high pressure vessel equipped with ports for base sparging of reactant gases, continuous liquid recirculation and gaseous and liquid product draws. During the hotwash cycle the reactor was ~60 % solvent filled and agitated with a five stage agitator assembly consisting of five downward pumping axial flow impellers.

Initial assessments of hotwash performance and required duration were made using a 40 % solvent filled 1 litre unbaffled CSTR with a six-blade downward pumping axial impeller in which a 37 mm x 17 mm cylindrical sample of the polymeric deposit had been affixed to the wall.

An unstructured tetrahedral and hexahedral mesh of ~3.5 million elements suitable for a steady state multiple reference frame (MRF) analysis[3][5] was created for the laboratory scale unit and a high quality unstructured hexahedral mesh of ~4.6 million cells suitable for a transient sliding mesh (SM) analysis[2][3] was fashioned from a dimensionally accurate CAD geometry for the analysis of the pilot scale unit. In both cases boundary layer cells were included to capture near wall viscous effects.

A RANS volume of fluids[1] multiphase approach was adopted to model the free surface flows assuming a Newtonian solvent using Fluent®. Turbulence effects were modelled using the realisable k-ε[6] and shear stress transport k-ω[4][5] models. Convergence of the 2nd order solutions was established by monitoring the total torque on the agitator and ensuring a decrease of residuals of at least 4 orders of magnitude – with the unsteady state SM analysis continued for ~32 revolutions of the impeller approximating fully developed flow.

Wall shear stress on the agitator and impeller blades in the pilot scale unit peaked at 45 Pa whilst the wall shear stresses on the external wall were significantly attenuated being of the order of 1 Pa. This was smaller that the 4 Pa calculated for the bulk of the polymer region in the laboratory scale simulation. The predicted free surface in the pilot scale model was in good agreement with indications derived γ-ray attenuation measurements though the vessel walls recorded during piloting.

A visual comparison of the development of the flow-fields derived with the realisable k-ε and shear stress transport k-ω models will be provided.

References

[1]. Hirt, C. W.; Nichols, B. D., Volume of Fluid (VOF) Method for the Dynamics of Free Boundaries. *J. Comput. Phys.*, (**1981**) **39** (1), 201-225.

[2]. Jakobsen, H. A., **2008**, *Chemical Reactor Modelling: Multiphase Reactive Flows.*, Springer-Verlag Berlin.

[3]. Marshall, E. M. and A. Bakker, **2004**, *Computational Fluid Mixing. In Handbook of Industrial Mixing: Science and Practice.* (pp. 257-343), E. L. Paul, V. Atiemo-Obeng and S. M. Kresta Eds., John Wiley and Sons, Inc., Hoboken, New Jersey.

[4]. Menter, F. R., Two-Equation Eddy-Viscosity Turbulence Models for Engineering Applications. *AIAA J.*, (**1994**) **32** (8), 1598–1605.

[5]. Moilanen, P.; Laakkonen, M.; Aittamaa, J., Modeling Aerated Fermenters with Computational Fluid Dynamics., *Ind. Eng. Chem. Res.*, (**2006**) **45** (25) , 8656-8663.

[6]. Shih, T.-H.; Liou, W. W.; Shabbir A.; Yang, Z.; Zhu, J., A New k-ε Eddy-Viscosity Model for High Reynolds Number Turbulent Flows - Model Development and Validation., *Comput. Fluids*, (**1995**) **24** (3), 227–238.

OP-I-21

IDENTIFICATION OF RHEOLOGICAL PARAMETERS FOR ENZYMATIC HYDROLYSIS OF LIGNOCELLULOSIC BIOMASSES VIA CFD AND EXPERIMENTS

Danilo Carvajal, Daniele Marchisio, Nunzio Russo, Debora Fino

Dipartimento di Scienza dei Materiali e Ingegneria Chimica - Politecnico di Torino,
Corso Duca degli Abruzzi 24, 10129 Turin – ITALY
corresponding author: debora.fino@polito.it

Enzymatic hydrolysis is a key step in the production of ethanol from lignocellulosic biomasses [1] and many of the relevant mixing issues, related for example to the contact between the biomass and the enzyme, can be addressed through simulations, if a reliable rheological model is provided. The lignocellulosic slurry (processed during hydrolysis) presents a non-Newtonian behavior, of viscoplastic type, which is very difficult to characterize with standard rheological measurements [2]. To overcome this problem, in this work computational fluid dynamics (CFD) is used in combination with experiments, carried out on a laboratory scale anchor reactor, to identify rheological parameters by employing the Herschel-Bulkley model. The methodology was firstly validated by using a fluid with known rheological behaviour (i.e., aqueous solutions of guar-gum) and was then applied to our test material: Arundo pretreated by steam explosion. Three-dimensional CFD simulations and experiments on the anchor reactor were carried out under different Arundo concentrations (18 - 35% w/w), stirring velocity (12 – 200 rpm) and hydrolysis time (0 - 4 hr.). The CFD simulations were carried out by using the moving reference frame approach; great care was used in the development of the computational grid and in the solution of numerical issues.

The validation of the methodology through comparison with experiment data (for the guar-gum solution) resulted in very close agreement. The identification of the rheological parameters (and their time evolution during hydrolysis) was successful and resulted in good agreement with the similar data published in the literature. In all hydrolysis tests the yield stress decreases with time, which is a consequence of the reduction of solid concentration (Fig. 1). The decrease in flow behavior index values with time, reaching values close to the unity (Fig. 2), indicates the transition from a shear-thickening behavior to shear-thinning. As far as the consistency index is concerned, in most cases it increases over time (Fig. 3), as a result of the change of the physical-chemical characteristics of the slurry during the hydrolysis process. Future steps of this work involve the evaluation of different prototypes with the aim of designing a mixing efficient continuous hydrolysis reactor.

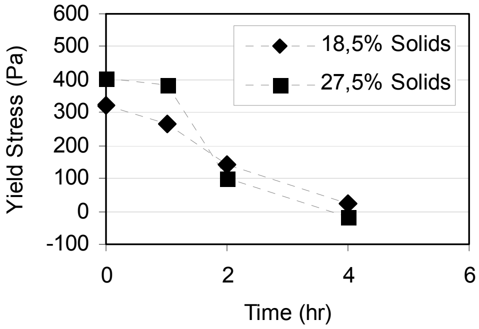


Figure 1: Yield stress evolution.

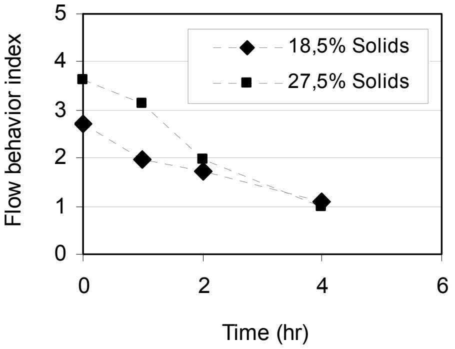


Figure 2: Flow behavior index evolution.

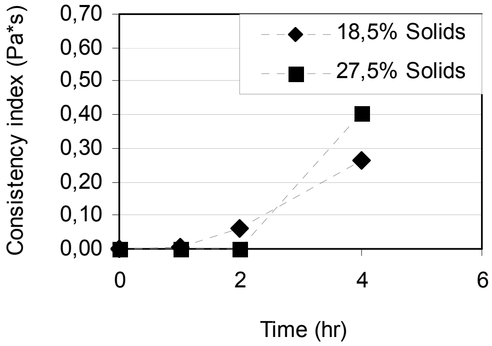


Figure 3: Consistency index evolution.

References

[1]. Zimbardi F., Viola E., Gallifuoco A., I de Bari, Cantarella M., Barisano D., Braccio G., Overview of the ethanol production. Report ENEA and University of L'Aquila, **2002**.

[2]. Pimenova N. & Hanley T. Effect of corn stover concentration on rheological characteristics. Appl. *Biochem. Biotechnol.*, **2004**, 114(1-3)347-360.

OP-I-22

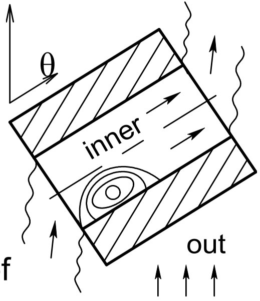
PRESSURE DROP IN BEDS OF RASCHIG RINGS AND MULTIHOLE PARTICLES

Voennov L.I., Zolotarskii I.A.

Boreskov Institute of Catalysis SB RAS, Novosibirsk 630090, Russia
zol@catalysis.ru

Raschig rings and multihole particles are widely used in practice as catalysts and packing material. This work is dedicated to investigation and obtaining physically grounded correlations of pressure drop in fixed beds composed of these materials with one-phase flow. There are two pure empirical correlations for calculation of pressure drop in a bed of Raschig rings [1,2] nowadays. Recent publications [3,4] suggest physical models of gas flow for this system. But all known correlations show not sufficient accuracy, especially for not isometric particles.

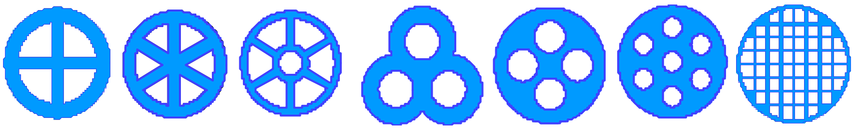
In this work a system is considered on two levels. A macro level uses a model of flow as two nonintersecting continuums with common boundaries. The whole gas flow is separated conditionally into circumfluent flow around external ring surface and flow inside channels. These flows are dynamically mated at channel boundaries, velocities and pressures being leveled. It is shown by applying an energy conservation law with further averaging that pressure drop in a bed of Raschig rings can be determined in the same way as for bulk particles, for instance, by well-known Ergun equation [5]. However, gas velocity in this equation should be equal not to velocity of the whole flow but average velocity of the flow between particles, hydraulic diameter to be defined without accounting for surface of holes.



A model of gas flow around a single particle is suggested on a micro level to determine gas velocity between particles. It is assumed that pressure drop in a gas stream flowing through a hole is balanced by difference in hydrostatic pressure in space between particles. Averaging equations of energy and mass conservation laws and assuming uniform distribution of rings in an orientation angle, a closed system of three equations is obtained which allows calculating pressure drop in a bed and averaged velocities of flows inside and about rings. These equations have only one new parameter, namely channel flow resistance coefficient resulting from diversion, narrowing and expansion of streams flowing through internal holes of rings.

A value of this coefficient was defined by fitting experimental data obtained with an unordered bed of different Raschig rings at wide range of gas velocities. Details of experiments will be presented in the report. It was found that the coefficient is equal to the Burke-Plummer constant 1.75. A mean-squared deviation of experimental and calculated values of pressure drop amounts to 6.2% being much less than for all known correlations.

In case of multihole particles there are more geometric parameters, thus the problem being fundamentally more complicated. Experiments with pressure drop measurements were carried out in a vertical tube with ID of 84 mm with particles shaped as shown on a figure. Gas velocity was varied from 0.2 to 3.0 m/sec. Ratio of tube diameter to maximum dimension of particles amounted 3.8-8.4.



In the same manner as for Raschig rings, a two-level model was considered for multihole particles. A gas stream flowing through all holes meets additional resistance being a baffle between holes. On the other hand, a circumfluent flow around particles does not interact with surface of these baffles. Taking into account these factors, by averaging equations of energy and mass conservation laws and assuming uniform distribution of rings in an orientation angle, a closed system of three simple equations is obtained. This system allows calculating pressure drop in a bed and averaged velocities of flows inside and about particles. The equations include as coefficients geometric parameters of particles, parameters of the Ergun equation for bulk particles (including effect of container walls according to [6]) and the obtained for Raschig rings averaged channel flow resistance coefficient. Thus, the system does not contain any additional empiric coefficient. It should be noticed that Ergun equation coefficients for bulk trilobes differ from that for cylinders.

A mean-squared deviation of experimental and calculated values of pressure drop amounts to 7-9% for all multihole particles under consideration. Thus, the developed method of pressure drop calculation gives estimations being in good agreement with experimental data obtained.

References

[1]. Brauer H., Druckverlust in Fullkorpersaulen bei Einphasenstromung, Chem.-Ing.-Techn. (**1957),** 29 (12) 785-790.

[2]. Zhavoronkov N.M., Hydrodynamic basis of scrubber processes and heat transfer in scrubbers. Moscow, Sovetskaya nauka, (**1944**), in Russian.

[3]. Smirnov E., Kuzmin V., Zolotarskii I., Radial Thermal Conductivity in Cylindrical Beds Packed by Shaped Particles, Chemical Engineering Reserch and Design, (**2004)**, 82(A2): 293-296.

[4]. Nemec D., Levec J., Flow through packed bed reactors: 1. Single-phase flow, Chemical Engineering Science (**2005**) 60, 6947-6957.

[5]. Ergun S. Fluid flow through packed columns. Chemical Engineering Progress, (**1952**), 48, 89-94.

[6]. Eisfeld B., Schnitzlein K., The influence of confining walls on the pressure drop in packed beds, Chemical Engineering Science (**2001**), 56, 4321-4329.

OP-I-23

TRANSITION AND SURFACE ENERGY EFFECTS ON PRESSURE DROP OF TAYLOR FLOW OF GAS-LIQUID MIXTURES IN MICRO CHANNELS

Abiev R.Sh.

St. Petersburg State Technological Institute (Technical University),
St. Petersburg, Russia, abiev_r@mail.ru

There are three methods of pressure drop simulation of Taylor flow in micro channels: homogenous model, Lockhart-Martinelli method, two-phase flow model. Only the latter could take into account velocity drift and velocity irregularity. It has been shown in many papers that mass transfer rate in micro channels have maximum when the bubbles and slugs are relative short. In this case the pressure drop in Taylor flow of gas-liquid mixture is much higher than in homogenous flow.

In this work we have proposed to take into account two factors: 1) non-parabolic velocity profile in liquid slugs; 2) additional energy loss due to gas-liquid interface permanent renewal during bubbles motion.

1) In the book [1] is a formula for the local pressure gradient for the undeveloped flow given.

$$\partial p / \partial x = -\left(8\mu U_s / R^2\right)\left[1 + \frac{1}{2}\sum_{m=1}^{\infty} \mathbf{exp}\left(-\nu\gamma_m^2 x / U_s R^2\right)\right], \tag{1}$$

where μ, ν – dynamic and kinematic viscosities of liquid; U_s – average liquid velocity; R – radius of channel; γ_m – roots of an 2nd order Bessel function.

Integrating equation (1) on the slug length L_s and using designation $a = 8\mu U_s / R^2$, $b = \nu\gamma_m^2 / U_s R^2$ for the capillary with N_{uc} unit cells we will get

$$\Delta p_c = -aN_{uc}L_s\left\{1 + \frac{1}{2bL_s}\left[1 - \mathbf{exp}\left(-bL_s\right)\right]\right\}. \tag{2}$$

2) A bubble is moving through a liquid slug with relative velocity $w = U_b - U_s$. A surface dF during time increment dt is in a tale part of bubble disappearing (dissipating to a heat) and in the same time in a nose part of bubble the equal surface dF is appearing. Hence, the rate of surface formation is

$$dF/dt = 2\pi R_b w, \tag{3}$$

where R_b – bubble radius. Energy supplied from without to capillary is

$$W_{\Delta F} = N_{uc}\sigma\, dF/dt = 2\pi R_b w\sigma L_c / L_{uc}, \tag{4}$$

where L_c – capillary length; L_{uc} – average unit cell length, σ – surface tension. Hence, corresponding pressure drop caused by permanent new surface formation

$$\Delta p_{\Delta F} = \frac{W_{\Delta F}}{\pi R^2 U_s} = \frac{2R_b}{R^2}\frac{w}{U_s}\frac{L_c}{L_{uc}}\sigma . \qquad (5)$$

Total pressure drop for gas-liquid Taylor flow in micro channels

$$\Delta p_{\mathrm{cal}} = \Delta p_c + \Delta p_{\Delta F} . \qquad (6)$$

A comparison of calculated and experimental [2] results illustrated by Fig. 1 shows acceptable fit for most of the data.

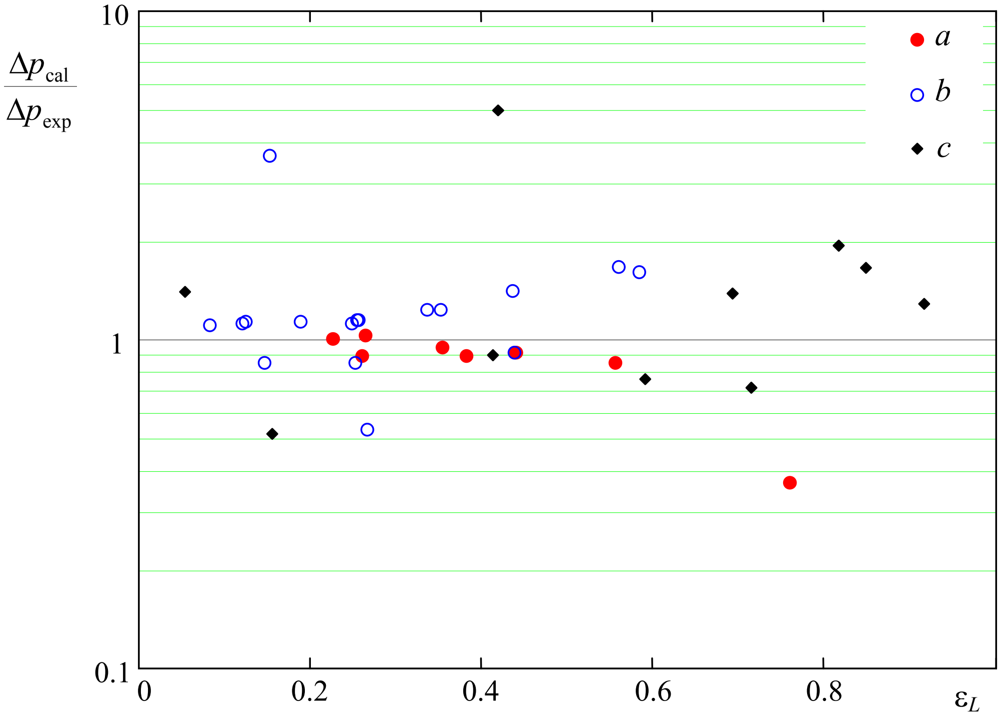


Fig. 1. Comparison of calculated (this work) and experimental data [2] of pressure drop for air-water mixture in capillaries with diameters of 0.92 mm (*a*), 2 mm (*b*), 3.02 mm (*c*) as a function of relative length of bubbles ε_L.

References

[1]. Slezkin, N.A., Dinamika vyazkoi neszhimaemoi zhidkosti (Dynamics of Viscous Incompressible Liquid), Moscow: Gos. Izd. Tekh.-Teor. Lit., **1955**.

[2]. Liu, H., Vandu, C.O., and Krishna, R., Hydrodynamics of Taylor Flow in Vertical Capillaries: Flow Regimes, Bubble Rise Velocity, Liquid Slug Length, and Pressure Drop, *Ind. Eng. Chem. Res.*, **2005**, vol. 44, p. 4884.

OP-I-24

THREE-DIMENSIONAL WATER VAPOUR TRANSPORT THROUGH POROUS PACKING OF SILICA GEL USING DIFFUSE NEAR-INFRARED TOMOGRAPHY

**Aiouache F., Nic An tSaoir M., McMaster M., Luis Abreu Fernandes D.,
Sa J., Hardacre C.**

*School of Chemistry and Chemical Engineering, Queen's University Belfast,
Northern Ireland, BT9 5AG, United Kingdom, E-mail: f.aiouache@qub.ac.uk*

Until recently, chemical gas-solid processes were described by 'single point' spectroscopy which led most fundamental understanding to be valid at separate space scales where averaged information and pseudo-homogeneous descriptions of species distribution, temperature and solid architecture were often used to simplify actual process heterogeneity. The developments of spatially resolved techniques however, have revealed that averaged performances of gas-solid processes in terms of activity, selectivity, or stability are the consequence of complex interplays between different physicochemical gradients at different length scales [1]. For instance, the fundamental understanding of the process of adsorption by using tomography techniques, i.e. magnetic resonance imaging (MRI) [2], microfocus X-ray [3], neutron tomography [4] or near infrared (NIR) imaging [5] allowed three dimensional (3D) distribution of the porosity, pore size, network tortuosity and capillary condensation to be mapped within macroscopic resolution from 0.01 to 10 mm of the silica. In this work, diffuse NIR tomography was used to retrieve local concentrations of water vapour in the vapour phase above a silica gel packing and the adsorbed phase of water vapour in the silica gel packing. The spatial resolution was of the order of hundreds of microns which allowed two space scales to be investigated: the first was at millimetre scale where the fluid flow, packing architecture, tube entrance and tube wall affected the isotropic distribution of water vapour; and the second was at sub-millimetres of a single pellet of silica gel, where intraparticle diffusion was the consequence. The locally interactions of convective and dispersive transport processes were used to obtain local dispersion and diffusion coefficients.

The experimental tomography technique relied on the principle of the so-called 'First generation tomography' where a parallel scanning was used. A NIR laser single source and a NIR detector were coupled together so that the detector was always facing the source. The source and detector were linearly rotated to acquire individual projections. The technique was based on transmission through water vapour medium and diffuse transmission through the solid packed bed adsorber. The polarised beam was collimated by a series of mirrors and cylindrical lenses and was collected by an image intensifying low light detector based focal planar array technology. The image reconstruction algorithm was based on the filtered back projection technique of adaptative algebraic reconstruction.

Circumference- averaged concentrations of water vapour in the packing and above the packing have shown different trends of the adsorbed and the gaseous phase of water vapour as the adsorption occurred. Unlike the cross-sectional expansion of adsorbed phase, the gaseous phase expansion above the packing occurred from the wall to the core centre of the packing bed. For any slice of the adsorbed phase however, the adsorbed phase extended through a periodic increase from the core packing to the wall and covered the whole of the cross-section of the bed. This behaviour is explained by the consequence of high velocities at the wall and periodic local porosity in the core centre of the adsorber which led to low residence times, and conversely high mass transfer, than that in the vicinity of the wall. The radially periodic increase was concentrated in the range of non-dimensional radial positions between 0.3-0.5 and 0.5-0.7 and these positions correspond in fact to low local porosity values foreseen by the literature models.

The experimental data of adsorbed water vapour, which counted for a voxel number of 64 x 64 x 460, radial resolution of 180 microns and axial resolution of 26 microns, were utilized to calculate the local dispersion coefficients directly by using the 3D partial differential equation (PDE) of the dispersion model. The inlet and outlet data of the packed bed were used as the boundary conditions for the PDE equation. The effective dispersion coefficient was adjusted by an optimisation algorithm in order to obtain the best fit between the measured and the calculated values at the outlet. The results of local values at the exit were compared to those obtained by classical methods of overall residence time distributions.

References

[1]. Coppens, M-O., Ind Eng Chem Res. **2005**, 14, 5011-5019.

[2]. S.P. Rigby and L. F. Gladden, Chemical Engineering Science, **1996**; 51, 10 : 2263-2272.

[3]. Roels, S. and Carmeliet J., International Journal of Heat and Mass Transfer. **2006**, 49, 4762-4772.

[4]. Asano, H., Nakajima, T., Takenaka, N., Fujii, T., uclear Instruments and Methods in Physics Research A, **2005**, 542, 241-247.

[5]. Salem, K., Tsotsas, E., Mewes, D., Chemical Engineering Science, **2005**, 60, 517-522.

OP-I-25

COMPARISON OF BUBBLE COALESCENCE MODELS WITH DATA FROM DIRECT COMPUTER SIMULATION AND EXPERIMENT

Boshenyatov B., **Semyanistij A.**

Russian Academy of Sciences, Institute of Applied Mechanics of RAS,
Moscow, Russia, bosbosh@mail.ru

Bubble column reactors are widely used in industry, but questions about their design and scale up remain. Modeling bubble coalescence is one of the most difficult problems, because the laws of coalescence are not studied sufficiently. The evolution of bubble size distributions at different heights of the column reactor are usually calculated on the basis of a one-dimensional population balance equation. The bubble coalescence and break-up mechanism is described by the introduction of two mathematical functions, which have two or more unknown parameters. The values of these parameters as recommended by various authors may differ from each other by several times [1].

The main objective of this paper is to improve our understanding of the fundamental mechanism of bubble coalescence.

For this purpose, a direct computer simulation program was developed for calculating the movement and coalescence of bubbles in a gas-liquid column reactor. The program allows to simulate the conditions for the generation of bubbles at the bottom of the column. Additionally, the initial distribution of bubble sizes may be specified. The three-dimensional trajectory of each bubble (straight or spiralling motion) and its speed are taken from the analysis of numerous experimental data.

The program calculates the gas volume fraction and bubble size distribution in discrete time steps. The result of each collision of bubbles is determined on the basis of the chosen model of coalescence.

Thus the program allows one to compare a known model of coalescence with experimental data for various parameters of bubble environments to determine their validity and applicability.

In order to analyse the degree of adequacy of the chosen model of coalescence to actual physical phenomena, the results of direct computer simulation were compared with experimental data. The experimental conditions should be such that coalescence plays the dominant role when the bubbles are floating up, while the effect of bubble break-up would be insignificant. Just such conditions were implemented in numerous and detailed experiments performed for the paper [2].

The results of experiments were compared with Direct Computer Simulation data, obtained using different generally accepted coalescence models and a novel bubble coalescence model based on critical Reynolds number [3].

References

[1]. Laakkonen, M.; Alopaeus, V.; Aittamaa, J. Validation Of Bubble Breakage, Coalescence And Mass Transfer Models For Gas-Liquid Dispersion In Agitated Vessel. *Chem. Eng. Science* **2006,** *61*, 218-228.

[2]. Brëoder, D.; Sommerfeld, M. Combined PIV/PTV-measurements for the analysis of bubble interactions and coalescence in a turbulent flow. *Can. J. Chem. Eng.* **2003,** *81*, 756-763.

[3]. Boshenyatov B. V. *Doklady Physics.* **2009,** *54*, No.7, 345–347.

OP-I-26

SOLID DISPERSION IN THE SLURRY REACTOR WITH MULTIPLE IMPELLERS

Klenov O.P., Noskov A.S.

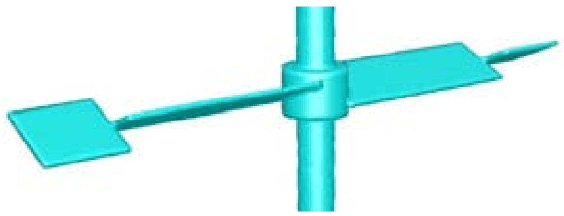
Boreskov Institute of Catalysis SB RAS, pr. Akad. Lavrentieva, 5,
630090 Novosibirsk, Russia. Fax:+007(383)3306878, klen@catalysis.ru

Multiphase slurry reactors are frequently encountered in the chemical and food industry. For example, multiple-impeller stirred tanks are the main units in the process of the selective hydrogenation of sunflower seed oil. Traditionally, a Raney nickel catalyst used as a solid phase.

Novel hydrogenation catalysts are developed at present time [1] to displace Raney Ni catalyst. Due to the difference in physical properties, such as a specific density of novel catalyst, the distribution of the solid particles of catalyst in the reactor should be reevaluated.

In recent years Computational Fluid Dynamics (CFD) simulation progressed into the reliable tool for investigation of multiphase flows with solid-liquid and gas-solid-liquid systems. Comparisons of the computational and experimental results have shown good agreement [2-3].

In the present work CFD simulation was used to predict a solid distribution in the stirred tank for cases with different specific density of the solid. The commercial CFD code (Fluent, Release 6.3) was used with the Mixture model of multiphase flows and the Multiple Reference Frame (MRF) model for swirling flow inside the slurry reactor. Some data of the mediums and stirred tank are shown in table.

Tank diameter	m	2.0	2-blades impeller 
Liquid volume	cub. m	12	
Number of impellers		5	
Number of blades		2	
Impeller diameter	m	1.3	
Liquid density	kg/cub.m	810	
Liquid viscosity	kg/(m*s)	0.049	
Solid particle diameter	m	0.0001	

A specific density of solid ρ_s and an agitation speed Ω were changed in the range 2300-8000 kg/m^3 and 50-200 rpm accordingly. Volume-weighted average volume fraction of the solid was equal $\phi_{s0}=0.0045$.

Results and discussion. A solid suspension in a tank stirred by five impellers has been studied and analyzed using CFD. Dimensionless volume fraction distribution of the solid $\bar{\phi}=\phi_s/\phi_{s0}$ as a function of the solid density is shown on Fig.1. The solid particles were introduced on upper surface of liquid at the start time. An impeller speed was equal Ω=100rpm. The results show that the solid density has a strong influence on the solid suspension. The value of the standard deviation of axial solid distribution was decreased from 0.585 to 0.081 when the solid density was increased from 2300 to 8000 kg/m^3.

An influence of the impeller speed on the solid suspension is shown on Fig. 2. The solid density was equal to 2300kg/m^3. A computational results show that increase of the agitated intensity as impeller speed from 50 to 200 rpm leaded to the deterioration of the axial solid distribution. The value of the standard deviation of the axial solid distribution was increased from 0.307 to 0.743. This result could be explained as the feature of intermixing flow in the stirred tank with five specific impellers and a manner of input solid into stirred tank on upper surface of liquid at the start time. Impellers separate tank on four domains with the swirling flow which are held up solid particles competing with gravitational force on solid suspension.

Conclusions. The distribution of the solid suspension in the height of the slurry reactor substantially depends on the solid density of the catalyst. The heavier particles create more uniform axial distribution of the solid suspension, if they were introduced on the upper boundary of liquid phase.

The increase of the mixing speed for the particles with solid density 2300kg/m^3 causes increase of the nonuniformity of the axial distribution.

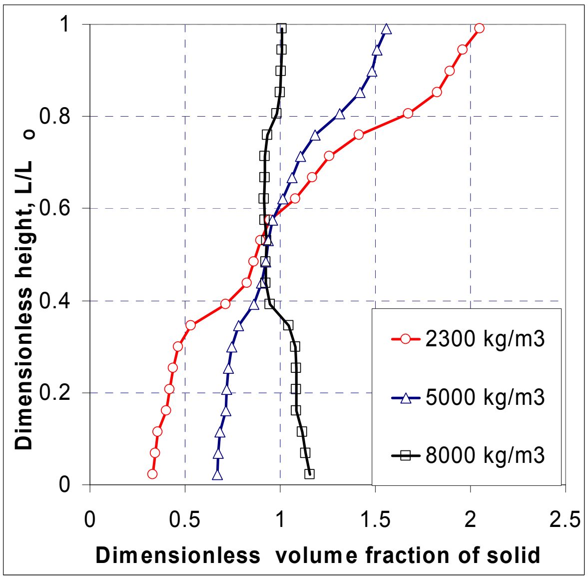


Fig. 1. The normalized axial solid concentration profiles $\bar{\phi}$ as a function of the solid density ρ_s. Ω=100 rpm.

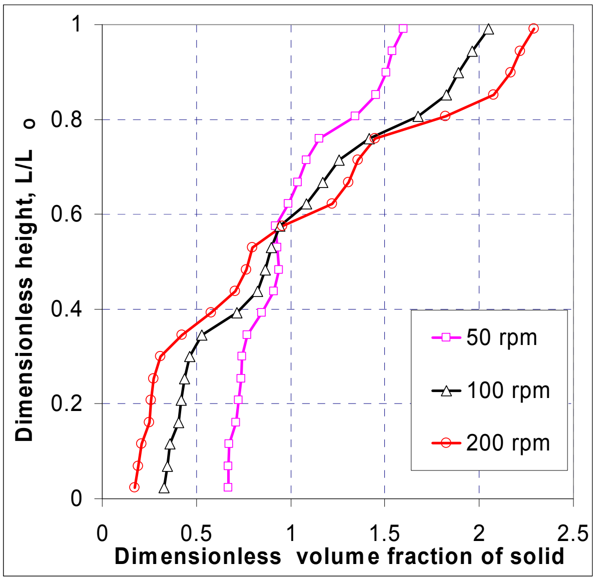


Fig. 2. The normalized axial solid concentration profiles $\bar{\phi}$ as a function of the impeller speed Ω. ρ_s=2300 kg/m^3.

References

[1]. V.A.Semikolenov. Russian Journal of Applied Chemistry, **1997,** Vol. 70, No. 5.

[2]. G. Montante, G. Micale, F. Magelli, A. Brucato. Trans IChemE, **2001**, Vol. 79, Part A, pp. 1005-1010.

[3]. D.A. Deglon, C.J. Meyer. Minerals Engineering. **2006,** Vol.19, pp. 1059–1068.

FORMALDEHYDE OXIDATION INTO FORMIC ACID ON A V/Ti CATALYST. DISCRIMINATION OF KINETIC MODELS

Danilevich E.V., Popova G.Ya., Andrushkevich T.V., Zolotarskii I.A., Ermakova A.

Boreskov Institute of Catalysis SB RAS, Novosibirsk 630090, Russia
yelenasem@catalysis.ru

Formic acid (FA) is produced commercially by a multi-stage liquid phase technology. The Boreskov Institute of Catalysis has developed the new one-stage gas-phase process of FA production by oxidation of formaldehyde (F) over the V_2O_5/TiO_2 catalyst [1]. The goal of this work was to evaluate a relible reaction kinetic model with well defined parameters.

Kinetic experiments were performed in a differential reactor with external circulation loop providing CSTR operation at temperature 105, 120, 130 and 140°C. Inlet concentrations of reagents were varied in the following ranges (in mol %): formaldehyde – 1.5-7.5, oxygen – 2.5-25.0, steam – 1-20, formic acid – 1-4. The catalyst was $11\%V_2O_5/90\%TiO_2$ with the BET of 140 m^2/g, .its fraction was 0.25-0.5 mm thus eliminating intraparticle diffusion limitation.

Based on experimental dependencies of partial reaction rates on reactant concentrations obtained and reaction mechanism of formic acid formation ascertained by IR spectroscopy method in situ [2], several surface reaction mechanisms were constructed. They differ in nature of active sites where particular reactions take place and kinds of some stages. Kinetic equations of product formation rates corresponding to these mechanisms were obtained by a graph theory [3].

Kinetic constants of all kinetic models along with activation energies were found by minimizing a sum of squared deviation of calculated and experimental concentrations. Minimization procedure is based on a Gauss – Marquardt gradient method. CSTR equations during iterations were solved by integration of corresponding differential equations till approaching a steady state.

Applying statistics methods, the kinetic model with best approximation of experimental data and with most reliable parameters was chosen. Kinetic equations for formation of formic acid and carbon oxides in this model are given below. Formic acid and carbon monoxide are formed on the same active site, while carbon dioxide is produced on sites of different nature.

$$w_{HCOOH} = \frac{K_1 \cdot P_{CH_2O}}{1 + K_2 \cdot \frac{(1 + K_3 \cdot P_{HCOOH})}{P_{H_2O}} + K_4 \cdot \frac{P_{CH_2O}}{P_{O_2}}}$$

$$w_{CO} = \frac{K_5 \cdot \frac{P_{HCOOH}}{P_{H_2O}}}{1 + K_2 \cdot \frac{(1 + K_3 \cdot P_{HCOOH})}{P_{H_2O}} + K_4 \cdot \frac{P_{CH_2O}}{P_{O_2}}}$$

$$w_{CO_2} = \frac{K_8 \cdot P_{CH_2O} + K_9 \cdot P_{HCOOH}}{1 + K_6 \cdot \frac{P_{CH_2O}}{P_{O_2}} + K_7 \cdot \frac{P_{HCOOH}}{P_{O_2}}}$$

Referencies

[1]. Andrushkevich T.V., Al′kaeva E.M., Popova G.Ya., Makarenko M.G., Zenkovets G.A., // Khim. Prom. 1996. Vol. 3. P. 21.

[2]. Popova G.Ya., Andrushkevich T.V., Zakharov I.I., Chesalov Yu. A. // Kinet. Catal. 2005. Vol. 46. P. 217.

[3]. Yablonskii G.S., Bykov V.I., Gorban A.N., Elokhin V.I., Comprehensive Chemical Kinetics in: R.G.Compton (Ed.), Kinetic Models of Catalytic reactions, vol. 32, Elsevier, Amsterdam/Oxford/New York/Tokyo, 1991 (Chapter 4).

OP-I-28

DEVELOPMENT AND APPLICATIONS OF THE MRI TOOLKIT IN CHEMICAL ENGINEERING AND HETEROGENEOUS CATALYSIS

Koptyug I.V.[1], Lysova A.A.[1,2], Kovtunov K.V.[1], Zhivonitko V.V.[1], Skovpin I.V.[1], Khomichev A.V.[1] and Sagdeev R.Z.[1]

[1]International Tomography Center SB RAS, Novosibirsk 630090, Russia,
E-mail: koptyug@tomo.nsc.ru
[2]Boreskov Institute of Catalysis SB RAS, Novosibirsk, 630090, Russia

In an ongoing study, we employ magnetic resonance imaging (MRI) to characterize *in situ* the heterogeneous hydrogenation of unsaturated compounds in an operating gas-liquid-solid trickle bed reactor with continuous or modulated reactant feed [1,2]. These studies allow one to map the distribution of the liquid phase within the catalyst bed, to visualize directly various dynamic processes, and to evaluate local reactant-to-product conversion. Many model studies of trickle bed and other multiphase reactors reported in the literature use “dummy” reactors, i.e., glass bead packs, water and air instead of the actual catalyst beds and liquid and gaseous reactants. In this respect, these MRI studies use a more realistic reactor model based on an actual catalytic process. The importance of this is addressed in a comparative study in which n-octene-1 is supplied to the bed of $Pd/\gamma\text{-}Al_2O_3$ catalyst, while the gas phase is either H_2 or N_2. The results clearly demonstrate that the distributions of the liquid phase within the catalyst bed are very different under reactive and non-reactive conditions. In particular, the exothermal hydrogenation of octene into octane leads to a pronounced non-uniformity of the liquid phase distribution in the catalyst bed. These qualitative observations are further supported by the semi-quantitative evaluation of the external liquid holdup and the internal wetting efficiency of the catalyst particles from the MRI data. Both quantities are observed to be measurably reduced under reactive conditions.

The distribution of the liquid phase in the catalyst bed is largely affected by the heat transport processes associated with the exothermal hydrogenation reaction. The MRI toolkit can be employed to obtain spatial temperature distributions as well. It is thus feasible to study mass and heat transport processes in an operating reactor using a single technique, i.e., under identical conditions and even at the same time. To achieve this, we continue to develop multinuclear and solid-state MRI approaches for the spatially resolved thermometry of operating catalytic reactors. The viability of the approach based on the direct imaging of ^{27}Al nuclei of the Pd/Al_2O_3 catalyst bed was demonstrated in the course of hydrogenation of propylene into propane [3]. One-dimensional profiles detected along the catalyst bed demonstrated temperature variations along the bed axis. More recently, these studies were extended toward the observation of dynamic heat transfer processes in individual catalyst particles and the two-dimensional temperature mapping of the catalyst bed. Hydrogenation of unsaturated compounds and the oxidation of H_2 were used for these initial model studies. It is expected that MRI could become a useful tool for the characterization of heat transport in operating catalytic reactors and for the visualization of hot spots formation and evolution.

Applications of the MRI toolkit are often limited by a relatively low sensitivity of the technique. For instance, MRI studies of hydrodynamics in micoreactors are difficult using conventional approaches. Hydrogenation reactions can be employed to develop hypersensitive MRI schemes. When parahydrogen is used in hydrogenation of unsaturated substrates, the products can exhibit an enhancement of their NMR signals by several orders of magnitude provided that the reaction mechanism ensures a pairwise addition of the two H atoms of the para-H_2 molecule to the same substrate. We have demonstrated recently that both immobilized metal complexes and supported metal catalysts are capable of producing significant signal enhancements when used in heterogeneous hydrogenation processes [4,5]. The signal enhancement levels achieved so far are about two orders of magnitude short of the possible limiting value, and catalysts more suitable for such applications are still to be identified. Nevertheless, we demonstrate that the signal enhancement already achieved allows one to successfully apply MRI to study various mass transport processes [6] including hydrodynamics in microfluidic chips.

References

[1] A.A. Lysova, I.V. Koptyug, A.V. Kulikov, V.A. Kirillov, R.Z. Sagdeev, *Topics Catal.*, **2009**, 52, 1371.

[2] A.A. Lysova, I.V. Koptyug, A.V. Kulikov, V.A. Kirillov, R.Z. Sagdeev, V.N. Parmon, *Chem. Engng J.*, **2007**, 130, 101.

[3] I.V. Koptyug, A.V. Khomichev, A.A. Lysova, R.Z. Sagdeev, *J. Am. Chem. Soc.*, **2008**, 130, 10452.

[4] I.V. Koptyug, K.V. Kovtunov, S.R. Burt, M.S. Anwar, C. Hilty, S. Han, A. Pines, R.Z. Sagdeev, *J. Am.. Chem. Soc.*, **2007**, 129, 5580.

[5] K.V. Kovtunov, I.E. Beck, V.I. Bukhtiyarov, I.V. Koptyug, *Angew. Chem. Int. Ed.*, **2008**, 47, 1492.

[6] L.-S. Bouchard, S.R. Burt, M.S. Anwar, K.V. Kovtunov, I.V. Koptyug, A. Pines, *Science*, **2008**, 319, 442-445.

Acknowledgments

This work was partially supported by the grants from RAS (5.1.1), RFBR (08-03-00661, 08-03-00539), SB RAS (67, 88), the program of support of leading scientific schools (NSh-7643.2010.3), FASI (state contract 02.740.11.0262) and CRDF (RUC1-2915-NO07). A.A. Lysova thanks SB RAS for the award of the Lavrentiev grant for young scientists.

MODELING OF RESIDENCE TIME DISTRIBUTION IN CORNING® ADVANCED-FLOW™ REACTOR

Woehl P., Lavric E.D., Kuandykov L.L.[1], Chivilikhin M.S.[1]

Corning SAS, Corning European Technology Center, 7 bis Avenue de Valvins,
77210 Avon, France;
[1]Corning SNG, Corning Scientific Center 26 A Shatelena str.194021, St.-Petersburg,
Russia; tel +7 812 329 2081, fax: +7 812 329 2061; e-mail: chivilikms@corning.com

Corning® Advanced-Flow™ reactor is a high-throughput, easily scalable reactor that can be customized to specific needs, enabling a cost-effective solution for a single reaction or a wide portfolio of reactions. The key component of the system is a specialty glass fluidic module. The module's structure, design and surface technology enable controlled, continuous and efficient streaming together of chemicals, resulting in excellent heat exchange performance and mixing quality. Glass fluidic modules are combined into specially engineered reactors that are customized to meet a wide range of chemical processing challenges. They are capable of managing multiple unit operations, and can be easily scaled to desired levels of production.

Contribution to numerical characterization of mixing in a reactor is provided by the quantified residence time distribution (RTD), thus allowing the process engineer to better understand mixing performance of the reactor. Many reactors are mixing-limited and/or mass-transfer limited and micro-mixing can be the critical element in contrast to RTD which addresses the macro-mixing.

Experimental studies on RTD in the fluidic modules used as components of Corning® Advanced-Flow™ reactors shown plug-flow like behaviour of these devices (Figure 1).

RTD, which provides a quantitative way to describe the time a unit volume of fluid spends in the reactor [1,2], has been analyzed by a series of numerical experiments with a full 3D Computational Fluid Dynamic model using FLUENT software. The developed approach includes two steps: steady-state calculations of the flow velocity pattern, and transient calculations of RTD [3]. In the transient calculation, the flow of a “tracer” through the fluidic module was monitored using previously computed velocity fields.

The RTD normalized step function (F) has been computed using predicted tracer concentration at the fluidic module outlet, like in experimental studies. The good agreement between CFD results and RTD experimental data validated modeling results. The results of the study suggest that CFD modeling can be a reliable alternative to tracer testing providing valuable informations when difficult media are involved (e.g. hazardous material, highly viscous liquids) and/or giving an insight on the flow in the process of designing new devices, saving time and money.

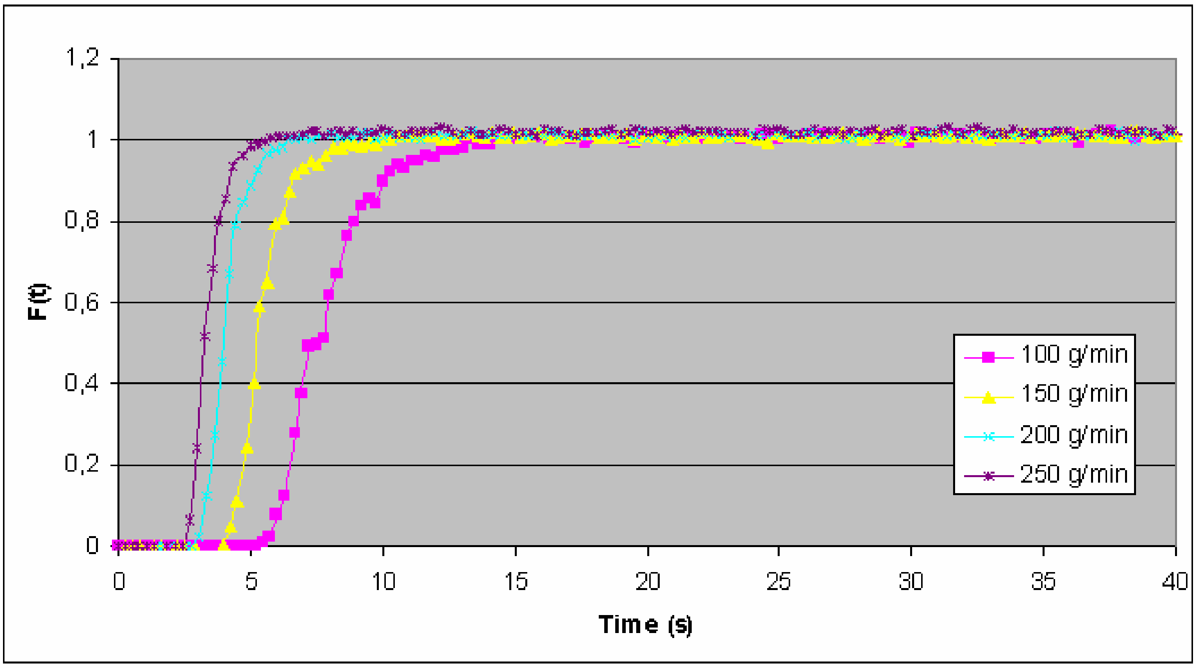


Figure 1. Experimental normalized tracer outlet concentration (the F curve)

References

[1]. George W. Roberts, Chemical Reactions and Chemical Reactors, John Wiley & Son Inc, 2009.

[2]. E.D. Lavric, P. Woehl, Advanced-Flow^{TM} glass reactors for seamless scale-up, Chemistry Today vol. 27 (3), 45-48, 2009.

[3]. H. Bai, A. Stephenson, J. Jimenez, D. Jewell, P. Gillis, Modeling flow and residence time distribution in an industrial-scale reactor with aplunging jet inlet and optional agitation, Chem. Eng. Res. Des. Vol. 86 (12), 1462-1476, 2008.

OXYDATIVE COUPLING OF METHANE IN THE FLUIDIZED BED REACTOR: INFLUENCE OF HYDRODYNAMICS AND KINETICS ON THE PRODUCT DISTRIBUTION

Jašo S., Arellano-Garcia H., Wozny G.

Berlin Institute of Technology, Strasse des 17. Juni 135, Sekr. KWT9 10619 Berlin,
stanislavjaso@mailbox.tu-berlin.de

Direct conversion of methane into other useful products is one of the most challenging subjects to be studied in heterogeneous catalysis. The Oxidative Coupling of Methane (OCM) process, in which methane is catalytically converted to C2 products (ethane and ethylene), is considered to be a suitable technology with high potential to exploit the huge amounts of natural gas as a feedstock. However, OCM is faced with two main drawbacks which are limiting its practical application. First one is the low yield of the reaction [1,2] which is limited to less than 30% so far. Other major drawback is the exothermicity of the reaction and severe hot spots [1].

Fluidized bed reactor was proposed by several authors [2,3] as the most promising reactor concept for the OCM. It was proven that operation with undiluted feeds of methane and oxygen is possible, with retaining nearly isothermal temperature profile [2,3,4]. However, yields of ethane and ethylene did not improve significantly, and they were in most cases similar like the ones obtained in the fixed bed reactor.

Scale-up and modelling of the fluidized bed reactors is presently done using either simple algebraic models or models based on the two phase theory. However, these models do not give insight into bed hydrodynamics, and are in all cases isothermal. Moreover, with such models it is impossible to investigate the influence of the distributor plate design, distributed feeding policy or effects of internals on the reactor performance.

In this contribution we developed a comprehensive 3D model (Fig. 1) for the fluidized bed reactor using a commercial CFD tool Fluent 6.3, based on the Eulerian granular flow model. Implemented kinetic model is the most comprehensive formal kinetic model for the OCM available in the literature [5], containing 10 parallel-series reactions. Reaction network and heat transfer coefficients had to be implemented through external UDF subroutines.

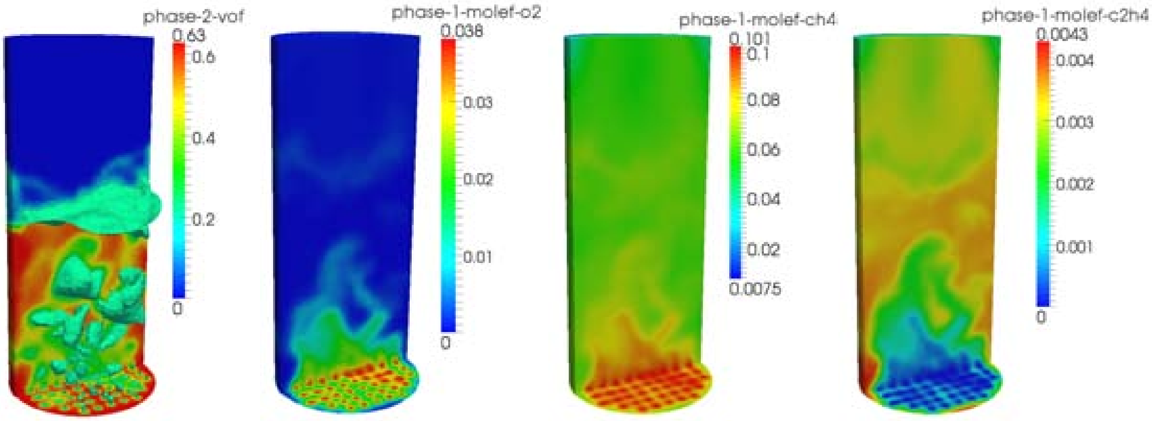


Fig. 1. Hydrodynamics and concentration profiles in the fluidized bed reactor for the OCM

Results of the simulation shows a typical “gulf streaming” of the gas phase, with a preferred flow-path through the reactor. A severe backmixing of solids and gas in the near wall regions is the main reason for reduced selectivity. Moreover, classical co-feeding policy has showed to give worse yields of ethane and ethylene.

Several case studies were investigated, each having its main impact on the bed hydrodinamics: ideal porous distributor plate, perforated plate distributor and distributed feeding policy through several feeding points. These cases showed different hydrodynamic pattern, which all affected different product yields, even with the same flow rate and same feed composition. Higher selectivity could be obtained only by suppressing gas back-mixing in the oxygen rich areas, thus preventing the product combustion.

Case studies conducted in this work enable further improvements in the fluidized bed reactor design, both in terms of feeding policy and reactor geometry. Reactor hydrodynamics has significant impact on its performance, and it has to be carefully considered when improved reactor performance is expected.

References

[1] F.M. Dautzenberg, J.C. Schlatter, J.M. Fox, J.R. Rostrup-Nielsen, L.J. Christiansen, Catal. Today 4 Vol.13 (1992) 503-509

[2] L. Mlezko, M. Baerns, Fuel Proc. Technol. 42 (1995) 217.

[3] G.Hutchings, in E.E. Wolf (Ed.), Methane Conversion by Oxidative Processes: Fundamental and Engineering Aspects, Van Nostrand Reinhold, New York, 1992, pp.

[4] L. Mleczko, U. Pannek, Ind. Eng. Chem. Res. 35 (1996) 54-61

[5] Z. Stansch, L. Mleczko, M. Baerns, Ind. Eng. Chem. Res. 36 (1997) 2568

Acknowledgements

The authors acknowledge support from the Cluster of Excellence "Unifying Concepts in Catalysis" coordinated by the Technische Universität Berlin and funded by the German Research Foundation - Deutsche Forschungsgemeinschaft.

OP-I-31

USE OF A HIGH-TEMPERATURE GRADIENT AS A THERMODINAMIC PUMP

Perko D.[1], **Hočevar S.**[1], **Levec J.**[1,2]

[1]Laboratory for Catalysis and Chemical Reaction Engineering, National Institute of Chemistry, P.O. Box 660, SI-1001 Ljubljana, Slovenia, david.perko@ki.si
[2]Faculty of Chemistry and Chemical Technology, University of Ljubljana, P.O. Box 537, SI-1001 Ljubljana, Slovenia

Based on the thorough CFD simulations and calculations a catalytic reactor with high temperature gradient is constructed. A high temperature gradient shifts the thermodynamic equilibrium of a reversible reaction to the right by continuously removing the formed products from the catalyst surface. We call this type of product removal the thermodynamic pump. Methanol synthesis is used as a model reaction.

The reactor consists of two horizontal plates (120 mm x 240 mm), separated by 2-10 mm: the upper one is covered by a thin layer (50-100 μm) of the methanol synthesis catalyst (Cu/Zn/Al) and heated up to 250-270 deg. C, whilst the lower one is cooled down to 30-50 deg. C. The gaseous phase flows between the plates in the laminar flow regime and is exposed to a huge temperature gradient. The hydrogenation of CO_2 to methanol and reverse water-gas shift reaction take place on the catalyst surface. The products, methanol and water, are continuously condensed on the cooled plate. This creates lateral gradients in their concentrations (Fig. 1), which drive the gaseous methanol and water from the catalyst surface into the bulk gas phase and further down to the cooled surface.

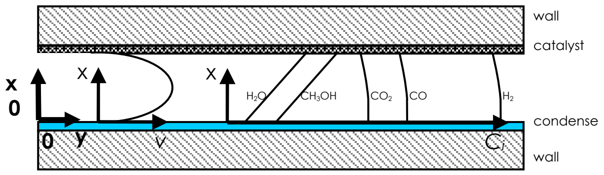


Fig 1. Schematic view of velocity and concentration profiles.

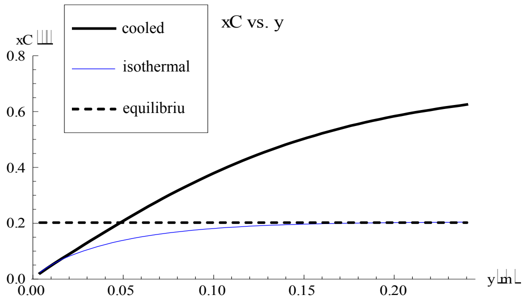


Fig 2. Conversion along the length of the reactor.

In order to determine enhancement of the conversion by the thermodynamic pump, its efficiency is going to be studied under different operating parameters (inlet gas-phase composition, pressure, temperature, gas-phase velocity, distance between plates) and compared with the system in which the bottom plate is not cooled.

Convection and diffusion within the space between the plates are estimated by the following equation

$$v\frac{\partial C_i}{\partial y} = D_{i,m}\frac{\partial^2 C_i}{\partial x^2} \tag{1}$$

which is solved for the appropriate boundary conditions:

$$C_i = C_i(x,y) \tag{2}$$

$$C_i(x,0) = C_{i,0}; \quad 0 \le x \le a \tag{3}$$

$$D_{i,m}\frac{\partial\ C_i}{\partial x}(a,y) = \left(\nu_{i,MeOH} r_{MeOH}(y) + \nu_{i,RWGS} r_{RWGS}(y)\right) d_{cat}\rho_{cat}; \quad 0 < y \le L \tag{4}$$

$$\frac{\partial\ C_i}{\partial x}(0,y) = 0 \quad \text{isothermal system} \quad 0 < y \le L \tag{5}$$

$$C_i(0,y) = \frac{x_i p_{i,eq}}{RT} \quad \text{cooled plate} \quad 0 < y \le L \tag{6}$$

Fig. 2 shows the calculated conversion of total carbon along the longitudinal coordinate for the following two cases: (i) the lower plate is cooled (boundary condition (6)); (ii) the lower plate is not cooled and the system is isothermal (boundary condition (5)).

The preparation of the 50-100 µm catalyst layer on the SS-316 plate by using the spraying method, is close to completion. The kinetic parameters of methanol synthesis on the same catalytic layer, also prepared by the spraying technique are studied in the mixing flow reactor. Four plates covered by this layer are used as an impeller in CSTR. Analysis is carried out by a GC/TCD.

Symbols:

a	distance between plates	r_{RWGS}	reaction rate of reverse water gas shift reaction
C_i	concentration	R	gas constant
$C_{i,0}$	inlet concentration	T	temperature
d_{cat}	thickness of the catalyst layer	V	velocity
$D_{i,m}$	diffusivity coefficient of i-component	x_i	mole-fraction in liquid
L	length of the reactor	X	x-coordinate
$p_{i,eq}$	vapor pressure of i-component	Y	y-coordinate
r_{MeOH}	reaction rate of methanol synthesis	ρ_{cat}	density of the catalytic layer
r_{RWGS}	rate of reverse water gas shift reaction	v_i	stoichiometric factor of i-component

ORAL PRESENTATIONS

SECTION II

Chemical Reaction Engineering and Reactors Design – Novel Approaches, Modeling, Scale-Up, Optimization:

New Designs of Chemical Reactors (Membrane Reactors, Microreactors, Structured Reactors, etc)

Novel Approaches in Chemical Reaction Processes Engineering (Unsteady-state and Transient Processes, Reverse-flow Operation, Sorption-Enhanced Reaction Processes, Multifunctional Reactors, Reaction-Separation Processes, etc)

TEMPERATURE RISE DURING REGENERATION OF DIESEL PARTICULATE FILTERS

Chen K., Martirosyan K.S. and Luss D.

Department of Chemical and Biomolecular Engineering, University of Houston,
Houston, Texas, USA, 77204, Dluss@UH.edu

The Diesel Particulate Filter (DPF) is the best existing technology for removal of particulate matter (PM). It is a wall-flow monolith consisting of many parallel extruded square porous ceramic cells. Every second channel is plugged at alternate ends. The exhaust gases enter the inlet channels and pass through the porous walls to adjacent outlet channels. The PM accumulated in the inlet channels is periodically removed by controlled combustion. A major technological challenge in the operation of diesel particulate filters (DPFs) is prevention of the occasional melting of the ceramic filters during regeneration (combustion of accumulated particulate matter). The cause of this melting is still an open question. Experiments and simulations indicate that during stationary regeneration (fixed feed conditions) the temperature rise is not sufficiently high to cause this ceramic Cordierite support melting (melting temperature ~1250°C). The reaction engineering literature include many studies of the wrong-way behavior in which a sudden decrease of the feed temperature to a packed bed reactor lead to a counter-intuitive temperature rise in the down stream section of the reactor. This led us to conjecture that the unexpected melting is due to a transient temperature excursion caused by a rapid shift of the driving mode of a car from normal driving to idle during combustion of the particulate matter. To test this conjecture we used Infra red imaging to measure the dynamic response of the spatio-temporal temperature on a planar DPF to a sudden change in the feed conditions. Both the experiments and numerical simulations revealed that the peak transient temperature after the change in the feed conditions was higher than the maximal temperature of the moving regeneration front under either the initial or final conditions. WE found that amplitude of the transient temperature rise depended on the direction in which the soot combustion front moved in the reactor and to the period between the formation of the combustion temperature front and the rapid change in the feed conditions.

ENTRAINER BASED REACTIVE DIVIDED WALL COLUMNS

Thotla S.[1], Freund H.[1], Sundmacher K.[1,2*]

[1]*Max Planck Institute for Dynamics of Complex Technical Systems, Magdeburg, Germany*
[2]*Process Systems Engineering, Otto-von-Guericke University, Magdeburg, Germany, *E-mail: sundmacher@mpi-magdeburg.mpg.de*

A reactive divided wall column (*RDWC*) integrates reactive distillation (*RD*) and downstream distillation into a single unit, which offers various advantages [1]. In case of non ideal vapor-liquid equilibrium (VLE), the mole ratio of reactants fed to the *RD* column depends on the azeotropic composition of the reactant(s) with the product(s) and the mutual solubility. In such cases, an azeotropic or an extractive distillation is required to further recover the reactant(s) and/or product(s). The case of using an entrainer in *RD* has already been analyzed [2] with the aim of maintaining the temperature in the reactive zone below the maximum allowable temperature for the catalyst.

In the present study, the use of a *RDWC* as a multifunctional reactor which performs both operations, i.e. *RD* and azeotropic distillation, is investigated. Two different entrainer based *RDWC* (i.e. *EBRDWC*) configurations for industrially important products such as ethyl acetate (EA) and n-propyl propionate (NPP) have been studied in detail by simulations. The *EBRDWC* configuration for EA production (Fig. 1) has a common top rectifying section which refluxes liquid to both sides of the dividing wall. In this case, EA itself acts as an entrainer. An NRTL VLE model and a concentration based kinetic model [3] have been used in the simulations. The effect of various operating parameters such as the reboiler duty, the number of reactive and non-reactive stages, common rectifying stages and the liquid split ratio have been studied to conceptually design the *EBRDWC*. The feasibility of a *RDWC* mainly depends on the pressure and temperature profiles on either sides of the dividing wall

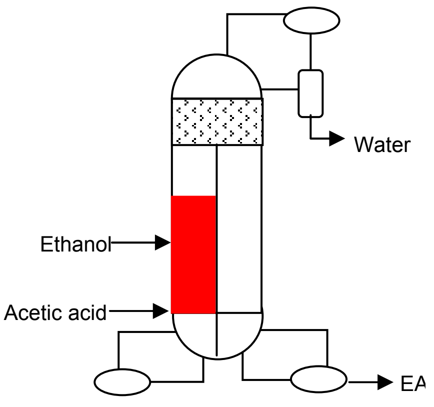


Fig. 1: *EBRDWC* for EA production

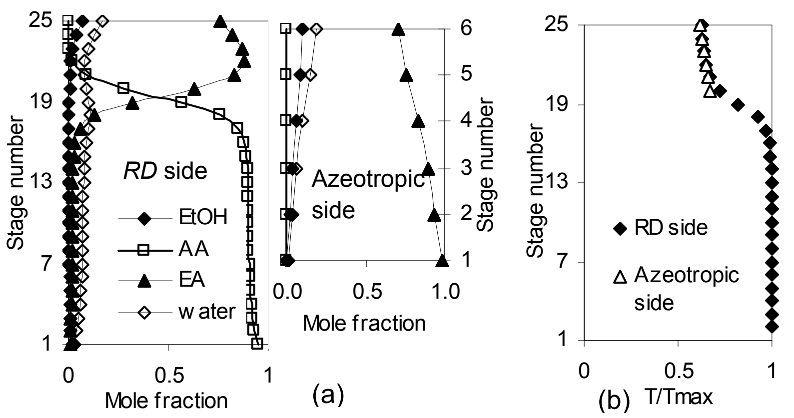


Fig. 2: (a) composition (b) temperature profiles of feasible *EBRDWC*

[4]. Similar temperature profiles can be obtained by modifying the feed location, the common rectifying stages and the liquid split ratio. Fig. 2 shows the temperature and composition profile for a feasible *EBRDWC*. From the simulation results it can be concluded that the production of EA is possible in an *EBRDWC* with nearly stoichiometric amount of reactants in the feed (ethanol/acetic acid~1.08).

For the case of NPP production, the *EBRDWC* configuration (Fig. 3) has a common top rectifying section and a common bottom stripping zone. In this case, methyl tert butyl ether (~0.001 kg/h) is used as an entrainer to break the 1-propanol-water-NPP azeotrope and to internally recycle 1-propanol and NPP. An activity based kinetic model [5] and the UNIQUAC VLE model is used to conceptually design the *EBRDWC* by operating the reactive side of the divided wall without liquid reflux from the common top section. The effect of the distributed propanol feed in the reactive side of the divided wall and of the number of common top rectifying stages has been studied to realize a feasible *EBRDWC* design (see Table 1). From these results, it is possible to produce NPP with stoichiometric amounts of reactants by performing *RD* and azeotropic distillation in a single unit without affecting the performance of either operation by an internal recycling of the reactant(s) and the entrainer.

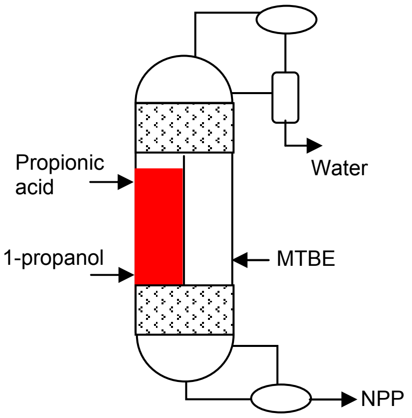


Fig. 3: *EBRDWC* for NPP production

Table 1: *EBRDWC* configuration for NPP

	Basis: 12 mol/hr of NPP	
	RD Side	Fractionator
Top common zone	5	
Bottom common zone	15	
Total stages	25	15
Reactive stages	15 (rectifying zone of *RD*)	
Catalyst loading (kg)	0.3	
Mole ratio	1	
Bottoms rate (mol/h)	12	
vapor split ratio	0.25	0.75
Reboiler duty (kW)	0.96 kW	

In the present work, it has been demonstrated that an *EBRDWC* is a novel intensified multifunctional reactor that allows for the production of industrially important chemicals with stoichiometric amounts of the reactants by breaking the azeotrope between the reactant(s) and the product(s) to achieve an internal recycling of the reactant(s).

References

[1]. Muller and Kenig, *Ind. Eng. Chem. Res.*, 46 (**2007**), 3709-3719.
[2]. Suman et al., *Ind. Eng. Chem. Res.*, 48 (**2009**), 9461-9470.
[3]. Tang et al., *AIChE J.,* 51 (**2005**), 1683-1699.
[4]. Kiss et al., *Chem. Prod. and Proc. Mod.*, 4 (**2009**), Article 2.
[5]. Duarte et al., *Inz. Chem. Procesowa*, 27 (**2006**), 273-286.

PECULIARITIES OF ETHANE OXIDATIVE DEHYDROGENATION IN MEMBRANE CATALYTIC REACTOR WITH SEPARATED FLOWS OF O_2 AND ETHANE

Kucherov A.V.[1], **Finashina E.D.**[1], **Orekhova N.V.**[2], **Ermilova M.M.**[2],
Kustov L.M.[1], **Tereshchenko G.F.**[2†]

[1]*Zelinsky Institute of Organic Chemistry, RAS, Leninsky Prosp. 47, Moscow, Russia*
E-mail: akuchero2004@yahoo.com
[2]*Topchiev Institute of Petrochemical Synthesis, RAS, Leninsky Prosp. 29, Moscow, Russia*

Possibility of application of the membrane technology for realization of productive and secure process of ethane oxidative dehydrogenation (EOD) is studied. This approach, with separated flows of O_2 and ethane, seems to be attractive from the safety point of view above all.

Layers of the Mo-V-Te-Nb-O_x catalyst was supported on the outer surface of the inert ceramic asymmetric porous membrane tubes with average pore diameter of 4.6 μm being made from α-Al_2O_3 by deposition of several layers of γ-Al_2O_3 and annealing at the temperature of 1250-1750°C. The transport characteristics of prepared membranes were determined on diffusion of He and Ar at room temperature. The permeability of membrane for helium was 4.5 mol/m^2s and that for Ar – 1.7 mol/m^2s, at the separation factor of this pair of gases being 2.6 (the Knudsen law factor 3.2).

The composite catalytic membranes were prepared by catalyst layer deposition from a fine powder suspension in water on the external surface of the porous ceramic tube and following drying in the air flow.

Catalytic membranes were tested in EOD at the temperatures of 320-460°C in the “tube in tube” glass reactor. Pure ethane was blowing the external (catalytic) surface of the membrane tube, and dosed oxygen supply to the catalytic layer was regulated by diffusion through the membrane from the inner void. In all experiments the main reaction products were ethylene and CO_2, with small admixture of CO. The switch of heterogeneous catalytic reaction to the gas phase oxidation was avoided at the conditions used in the membrane reactor testing.

Figure 1 illustrates catalytic properties of the membrane catalyst prepared by deposition of 220 mg of the Mo-V-Te-Nb-O_x active phase on the ceramic tube (d = 7.5 mm; l = 125 mm). The sample demonstrates high activity and selectivity

(Fig, 1 a, b) upon testing in conditions (C_2H_6 flow 19.2 cm^3/min; O_2 flow 4 cm^3/min) being similar to those used earlier upon standard testing in the gas mixture (Fig. 2 a, b).

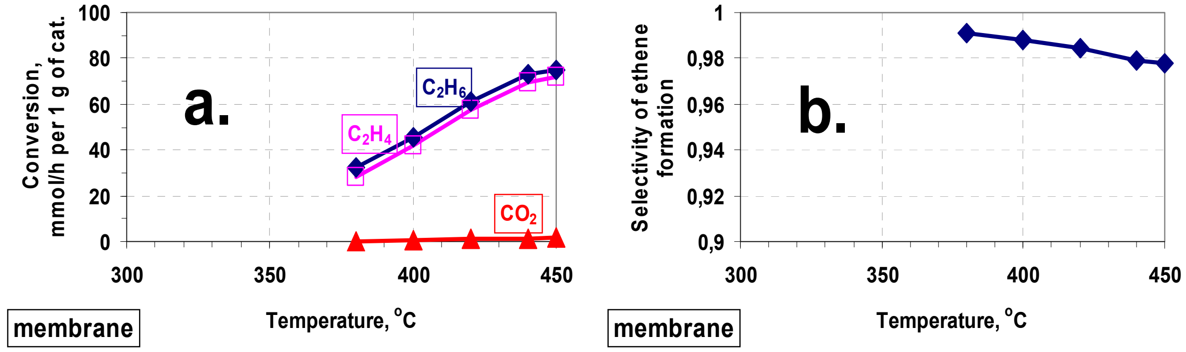


Fig. 1. EOD on the membrane Mo-V-Te-Nb-O_x/Al_2O_3 catalyst: (a) – ethane conversion; (b) – selectivity of ethylene formation.

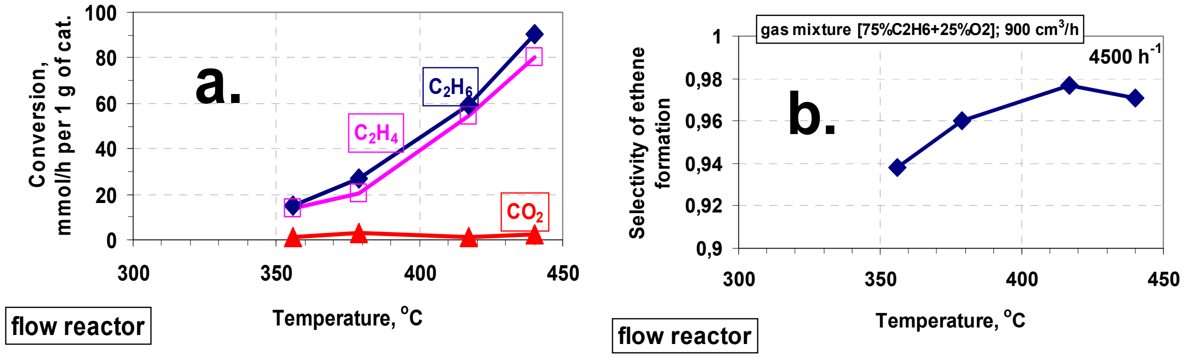


Fig. 2. EOD on the Mo-V-Te-Nb-O_x catalyst in flowing mixture [75%C_2H_6+25%O_2]: (a) – ethane conversion; (b) – selectivity of ethylene formation.

The catalytic data received upon variation of gas flow rates demonstrate that realization of EOD in the membrane mode, with separated gas flows, allows the practical use of [ethane : O_2] ratios, which are absolutely prohibited in the gas mixtures on considerations of safety. The one-pass conversion of ethane can be raised from 50% for ([ethane + oxygen] mixture) to 70% for the membrane process at the selectivity remaining on the level of ~95%.

Acknowledgements

This work was supported by the Program of Presidium RAS, project No.14.

OP-II-4

REPEATED OPTIMIZATION OF A FIXED-BED REACTOR FOR ETHYLENE EPOXIDATION

Xing-Gui Zhou, Xi-Yuan Qian, Ai-Hua Pan

State-Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China, E-mail: xgzhou@ecust.edu.cn

Ethylene epoxidation is one of the largest hydrocarbon partial oxidation processes in chemical process industry. Because of the typical wall-cooled reactor used for the reaction and the huge scale of the production, optimization of the reactor will bring in significant profit for the industry by lowing ethylene consumption or by increasing the ethylene peroxide productivity.

Optimization of ethylene epoxidation is difficult because the performance of the reactor is related to a number of factors. Apart from the six main components, i.e., ethylene, oxygen, ethylene oxide, carbon dioxide, water, and methane (as balance gas) that have effects on the catalytic reaction by competitive adsorption or by changing the explosive limit of the gas mixture, and the contacting time that changes ethylene conversion, chlorine is also introduced to adjust the activity and selective of the catalyst [1]. The most complicating factor in optimizing this process is catalyst decay which leads to a continuously decreasing catalyst performance. Accordingly the optimal operating conditions, especially the reaction temperature, should be changed with time.

In this communication, an approach for repeated optimization of the process is presented. A steady-state one-dimensional plug-flow model is used for the reactor, and a generalized power law expression [2] is used to account for the catalyst deactivation. The reactor is repeatedly optimized in the following way:

(1) Determine the temperature profile from the present time to the end of the catalyst operation, under the constraints of constant daily productivity and maximum allowable catalyst-bed temperature;

(2) Optimize the inlet composition (outside the explosive envelope) and the space velocity to maximize (a) the productivity, or (b) the selectivity (with a preset productivity);

(3) Repeat the first step with the optimized inlet composition, the space velocity and the maximized or preset productivity.

In the second step optimization, if the productivity is set, the set productivity can be increased until the temperature profile determined in the first step optimization violates the maximum allowable catalyst-bed temperature constraint. Simulation studies show that maximizing the selectivity with step-wise increased productivity is equivalent to maximizing the productivity.

This optimization approach has been integrated in a software package and applied on an industrial fixed-bed reactor. The amount of chlorine addition was not used as a manipulated variable because it was added according to the variation of ethane concentration in the gas mixture. The kinetics of ethylene epoxidation, combustion and catalyst deactivation were determined off-line by using the plant data collected over a period of time, and the optimization package was then used to find the best operating variables, which were then applied to the reactor. The reactor was repeatedly optimized for a year, which increased the average selectivity of about 0.5%.

References:

[1]. D. Torres, F. Illas, R.M. Lambert, Towards an understanding of promoter action in heterogeneously catalyzed ethane epoxidation: Why chlorine is the best halogen, J. Catalysis, 260 (2008) 380-383.

[2]. C. H. Bartholomew, Mechanisms of catalyst deactivation. Appl .Catal. A: General, 212 (2001) 17-60.

Acknowledgements:

The authors are grateful for the financial support by Sinopec.

OP-II-5

SEPARATION OF GASEOUS OLEFIN/PARAFFIN MIXTURES BY REACTIVE ABSORPTION IN A MEMBRANE CONTACTOR

Ortiz A., Fallanza M., Gorri D., Ortiz I.*

*Departamento de Ingeniería Química. Universidad de Cantabria. Avda. de los Castros s/n. 39005 Santander, Spain: *e-mail: ortizi@unican.es*

The separation of olefins and paraffins is of primary importance in the chemical industry. Traditional systems, like low-temperature distillation, are expensive, energy-consuming and voluminous process equipment due to the similarity in boiling point of olefin and their corresponding paraffin. Therefore, alternative, less-expensive separation methods are required. Among a number of alternatives separation processes, reactive absorption of olefins from olefin/paraffin mixtures using a silver salt solution as absorption liquid in a gas/liquid membrane contactor may be attractive in this respect.

The two main advantages of membrane contactors over conventional two-phase contacting-based separating devices are their non-dispersive character and their high efficiency in terms of mass transfer, due to increased specific area of contact. Due to this non-dispersive contact, the flow-rates on both sides of the membrane may be set independently, as long as the pressure conditions along the contactor module assure the stabilization of the two-phase interface. Additionally, foaming in gas–liquid separation processes is minimized. The high efficiency in terms of mass transfer is due to high (and known) interfacial areas, which lead to more compact equipments. Also, scaling up is easy due to the modular character of the equipment.

Solvents with high olefin-capacity, selectivity and resistance to contaminants and process conditions are still needed. Room Temperature Ionic liquids (RTILs) can be use as reactive absorption solvents for olefin/paraffin separations because of its ionic and organic character together with its renowned and remarkable properties. In this work, $BMImBF_4$ has been selected for experiments because of absorption selectivity for propylene over propane and it is able to dissolve a suitable silver salt ($AgBF_4$), allowing to absorb propylene due to reversible complexation of silver ions with unsaturated olefinic double bonds.

In previous works, the physico-chemical characteristics of the system, absorption equilibrium and kinetics of the reaction between propylene and Ag^+-$BMImBF_4$ mixtures, required to design industrial separation processes with gas-liquid membrane contactors were studied by our research group [1,2]. In this study, a membrane contactor was used in the propane/propylene selective absorption. A propylene-containing mixture was contacted with the ionic liquid/silver salt solution, and propylene was absorbed. After propane was removed, propylene was recovered by desorption. Concerning the membrane contactor unit, a hollow-fiber module (Enka-Mycrodyn) with hydrophobic microporous polypropylene hollow-fiber membranes, with a nominal pore size of 0.20 μm, was used. The liquid absorbent selected circulated through the shell-side, because such a viscous liquid would cause a too high pressure drop if circulated in the tube side.

We include both experiments and a theoretical study devoted to the analysis of the transport phenomena that occur in the membrane contactor. The experimental study analyzed the influence of operation variables such as gas feed composition (30%-70% v/v of C_3H_6) and silver salt concentration on the absorption flux of propylene at room temperature. The viability of this technology to carry out the separation was proved; it was found that the main resistance to mass transport was located at the liquid side.

References

[1]. A. Ortiz, A. Ruiz, D. Gorri, I. Ortiz, Room temperature ionic liquid with silver salt as efficient reaction media for propylene/propane separation: Absorption equilibrium, Sep. Purif. Technol. **(2008)**, 63, 311-318.

[2]. A. Ortiz, L. M. Galán, D. Gorri, A.B. de Haan, I. Ortiz, Kinetics of reactive absorption of propylene in RTIL-Ag+ media, Sep. Purif. Technol. (accepted, **2010**).

Acknowledgements:

This research has been funded by the Spanish Ministry of Education and Science (Projects CTQ2008-00690/PPQ and CTM2006-00317).

MICROCHANNEL REACTOR WITH A Cu/CeO_{2-x} CATALYTIC COATING FOR PREFERENTIAL CO OXIDATION. OPERATION, MODELING, AND SCALE-OUT

<u>Snytnikov P.V.</u>[1,2], Potemkin D.I.[1,2], Rebrov E.V.[3],
Hessel V.[3,4], Schouten J.C.[3], Sobyanin V.A.[1,2]

[1]Boreskov Institute of Catalysis SB RAS, Pr. Lavrentieva, 5, Novosibirsk, 630090, Russia, pvsnyt@catalysis.ru
[2]Novosibirsk State University, Pirogova St., 2, Novosibirsk, 630090, Russia
[3]Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, the Netherlands
[4]Institut fur Mikrotechnik Mainz GmbH, Carl-Zeiss-Strasse 18-20, 55129 Mainz, Germany

Preferential CO oxidation (PrOx) is one of the promising methods for CO removal from hydrogen-rich gas mixtures produced by hydrocarbons conversion processes. Several advantages of applying microreactors in comparison with conventional fixed-bed technology for the highly exothermic CO PrOx reaction were demonstrated in different studies [1-5]. A high rate of heat removal from the thin catalytic film deposited onto the microchannel walls allows for near-isothermal operation and in this way prevents the onset of side reactions (viz., hydrogen oxidation or reverse WGS) and extends the operational window [2-4].

According to our previous work [4], the copper-cerium oxide catalytic system is a very promising one for efficient CO removal from a hydrogen-rich gas using microreactor technology. Simple sandwiched (two-plate) and laser-welded microchannel reactors were used for catalyst testing. The catalyst performance for preferential CO oxidation in H_2 excess was studied in a flow setup with on-line chromatographic analysis of the reaction products. Catalytic performance of the microchannel reactors were checked using model feeds at WHSV = 50÷500 L $g^{-1}h^{-1}$ and temperature 100÷300°C. The washcoated catalyst in the microchannel reactor showed high activity and selectivity. The CO concentration was decreased from 1 vol% to 10 ppm at a selectivity of 60%, at a temperature of 190°C, and a WHSV of 55 L $g^{-1}h^{-1}$. The CO outlet concentration and the reactor temperature increased when the WHSV was increased from 50 to 500 L g^{-1} h^{-1}. An increase of the O_2 concentration from a 1.2 to 3 fold excess reduced the CO concentration to 10 ppm in a broad temperature interval at WHSVs up to 275 L g^{-1} h^{-1}.

Catalytic experiments have been performed that allowed determining the apparent activation energy of the reactions of CO and H_2 oxidation, the reaction orders with respect to O_2 and CO. Results of numerical modeling of the PrOx reaction over Cu/CeO_{2-x} catalysts using estimated kinetic parameters were in a good agreement with the experimental data.

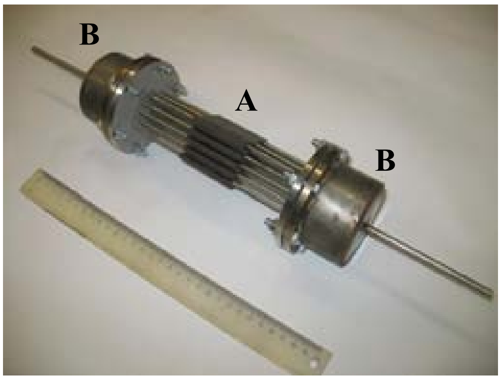


Figure 1. Microreactor assembly (A) with gas distribution fittings (B).

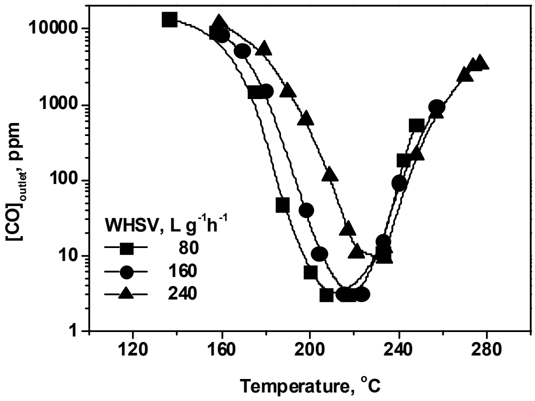


Figure 2. The CO outlet concentration in the preferential CO oxidation as a function of the reactor temperature at a WHSV.
The reformate composition is: 1.5 % CO, 2.25 % O_2, 57 % H_2, 10 % H_2O, 20 % CO_2, with He as balance.

An authothermal preferential CO oxidation device consisting of an array of 26 microchannel reactors connected in parallel was designed for operation with a $100W_e$ PEM FC system (Fig.1). In this design, the external surface area of the individual microchannel reactors was used for heat-exchange with the environment to maintain the desired operation temperature. Thus, the heat flux via the external surface areas of the parallel microchannel reactors and the fittings was equal to the heat produced by the reaction. The carbon monoxide concentration in a realistic reformate gas was reduced from 1.5 vol.% to 10 ppm (Fig 2.) at an oxygen to carbon monoxide ratio of 1.5 within the temperature range of 230 - 240 °C, which is close to the temperature of the low temperature water gas shift reactor. This facilitates the assembling of the CO PrOx and WGS microreactors without the need for an intermediate heat-exchanger to achieve higher efficiencies in the overall fuel processing.

References

[1]. E.R. Delsman, B.J.P.F. Laarhoven, M.H.J.M. de Croon, G.J. Kramer, J.C. Schouten, Chem. Eng. Res. Des. **(2005)** V.83 P.1063.
[2]. X. Ouyang, R.S. Besser, J. Power Sources **(2005)** V.141 P.39.
[3]. X. Ouyang, L. Bednarova, R.S. Besser, P. Ho, AIChE J. **(2005)** V.51 P.1758.
[4]. P.V. Snytnikov, M.M. Popova, Y. Men, E.V. Rebrov, G. Kolb, V. Hessel, J.C. Schouten, V.A. Sobyanin, Appl. Catal. A **(2008)** V.350 P.53.
[5]. G. Chen, Q. Yuan, H. Li, S. Li, Chem. Eng. J. **(2004)** V.101 P.101.

Acknowledgements

The work was partially supported by grant “UMNIK“ of the FASIE, MK-5602.2010.3 (grant of the President of the Russian Federation) and GC №P185 of FFP “SSESIR 2009-2013”.

OP-II-7

THE ROLE OF CATALYST ACTIVITY ON THE TRANSIENT AND STEADY STATE MODELING OF AN INDUSTRIAL PACKED BED CATALYTIC REACTOR WITH LOW d_t/d_p: o-XYLENE PARTIAL OXIDATION ON A V/Ti CATALYST

Castillo-Araiza C.O. and **Lopez-Isunza F.**

Departamento de Ingeniería de Procesos e Hidráulica, Universidad Autónoma Metropolita Unidad Iztapalapa, México. E-mail: coca@xanum.uam.mx

Travelling hot spot and multiple steady states have been observed in non-adiabatic fixed bed catalytic reactors for strongly exothermic reactions when operating conditions change drastically, i.e., cooling temperature[1-2]. In particular, for the partial oxidation of o-xylene to phthalic anhydride on an industrial V_2O_5/TiO_2(Anatasa) catalyst, this behavior has been related to reversible and irreversible catalyst deactivation[1-3]: the former being attributed to the combination of several mechanisms such as an over-reduction of vanadium, deposition of carbonaceous materials and strongly absorbed species; and the latter being linked to structural changes in the catalyst itself such as a TiO_2 anatase-rutile transformation, a decrease in surface area with loss in activity and a decrease in a promoter composition at the catalyst surface. Although the modeling of this kind of systems/phenomena has been performed since 1946 [4], an agreement between predicted and observed temperature and yield profiles has not been satisfactory [1-2, 5]. Some studies have shown that these simplified models cannot describe the reactor performance quantitatively, even though independently determined intrinsic kinetic and transport parameters are used [3]; besides, several authors have pointed out that the main aspects to be addressed in the modeling of this class of reactors are related to understand/determine [1-3, 6]: *the role of hydrodynamics on heat transport phenomena; and the kinetics of the catalytic and deactivation reactions*.

The aim in the present work is to develop/propose a modeling approach to predict observations in steady and transient state for catalytic reaction systems where a highly exothermic reaction takes place: an adequate consideration of hydrodynamics and the reversible and irreversible catalyst deactivation into the developed reactor model is essential on heat and mass transport description.

The experimental system is a single-tube industrial scale packed bed catalytic reactor, packed with spheres (d_t/d_p~3) of a non-porous commercial V_2O_5/TiO_2 (Anatasa) [7]. The cooling system consisted of an air-agitated bath of molten salt at temperatures operating in the range 665-675°K, and the o-xylene feed to air flow rate ratio was 44 Ng/m^3. This system when is operated either at steady or transient state is modelled by means of a two dimensional pseudo-heterogeneous model: an experimental study in absence of reaction together with the corresponding modeling approach is used to characterize hydrodynamics and heat transport processes; the reversible catalyst deactivation, considered via an oxide-reduction dynamics, together with an imposed activity profile are implemented into a well-known Calderbank et al., kinetic model [8]. The resulting developed reactor model is tested against steady state observations, vides Figure 1.a., and used to predict dynamic observations occasioned when bath temperature is increased 10° K (1°/min) after the first steady state has been reached, vide Figure 1.b. The incorporation of the redox dynamics into the Calderbank kinetics makes this model to lead to better predictions of temperature observations than the Calderbank's model on its own. The transient simulation shows that the developed model is able to predict travelling temperature profiles observed during the dynamic operation of this reactor.

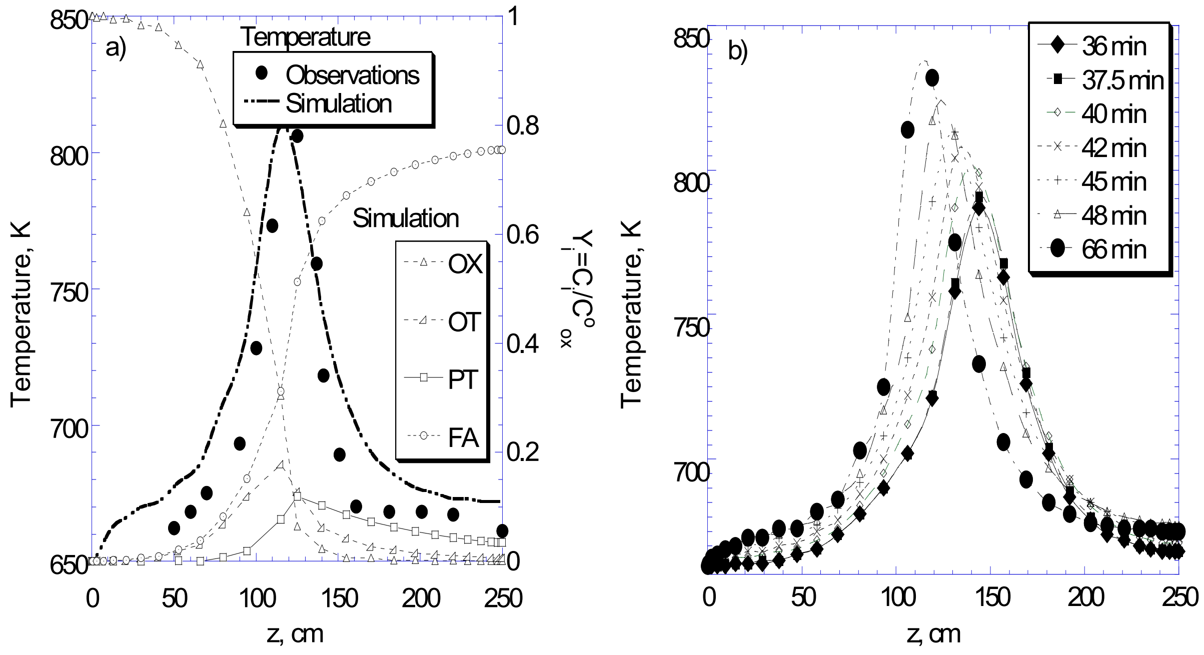


Figure 1. a)Temperature predictions at steady state. b) Temperature predictions at transient state: bath temperature is increased 10°K after the first steady state has been reached.

References

1. Mongkhonsi, T., Kersenbaum, L. Applied Catalysis A: General, 1998. **170**: p. 33.
2. Lopéz-Isunza, F., Kershenbaum, L.S. Chemical Engineering Science, 1992. **47**(9-11): p. 2817.
3. Castillo-Araiza, C.O., *Modelling of an industrial scaled o-xylene partial oxidation packed bed catalytic reactor*. 2008, Ph.D,Metropolitan Autonomous University-Iztapalapa: México. p. 263.
4. Tasker, G.J.H. Trans. Inst. Chem. Engrs. (London), 1946. **24**: p. 84-89.
5. Anastasov, A.I. Chemical Engineering Journal 2002. **86**: p. 287-297.
6. Papageorgiou, J.N., Froment, G.F. Chemical Engineering Science, 1995. **50**(19): p. 3043-3056.
7. López-Isunza, F., *Steady state and dynamic behavior of an Industrial fixed bed catalytic reactor.* 1983, Imperial College, University of London.: Londo, England. p. 299.
8. Calderbank, P.H., Chandrasekharan, K., Fumagalli, C. Chemical Engineering Science, 1977. **32**: p. 1435-1443.

OP-II-8

MATHEMATICAL MODELING OF β-PICOLINE OXIDATION TO NICOTINIC ACID IN MULTITUBULAR REACTOR: EFFECT OF THE RESIDUAL GAS RECYCLE

Ovchinnikova E.V.[1], **Vernikovskaya N.V.**[1,2], **Andrushkevich T.V.**[1], **Chumachenko V.A.**[1]

[1]*Boreskov Institute of Catalysis SB RAS, address: pr. Akademika Lavrentieva, 5, Novosibirsk, 630090, Russia; e-mail: evo@catalysis.ru, ph.: +7 383 3269412*
[2]*Novosibirsk State University, Pirogova St., 2, Novosibirsk, 630090, Russia*

Nicotinic acid (NA) forms directly from β-picoline (βP), as well as through intermediate formation of pyridine-3-carbaldehyde [1]. When conversion of βP (X) grows, selectivity to NA (S_{NA}) drastically decreases due to the parallel route of oxidation of NA to COx (Fig.1).

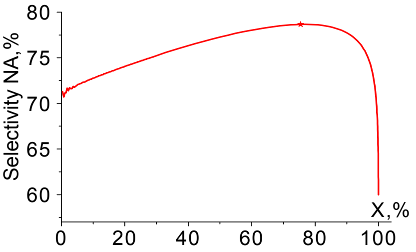


Fig.1. S_{NA} *vs.* X in multitubular reactor

Our former kinetic studies of βP oxidation over V_2O_5–TiO_2 catalyst [2] revealed the key influence of components O_2/βP ratio on the activity, selectivity and stability of the catalyst [1, 3]. This fact can be satisfactorily described in terms of kinetic model [1]. On the grounds of dependence of NA accumulation rate and of selectivity S_{NA} and S_{COx} on the ratio of the initial concentrations O_2/βP, we have shown that the reaction of βP selective oxidation should be performed at O_2/βP=11÷20 (Fig.2). Within this interval, the rate of NA production increases, while above 20 the yield of complete oxidation products COx increases, and below 11 the catalyst reduction followed by its inactivation takes place [1, 3].

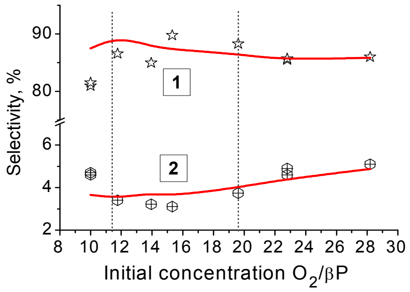


Fig. 2. S_{NA} (1) and S_{CO2} (2) vs.O_2/βP at X≈60%. *Lines – prediction, points – experiment.*

The use of recycling is widely known. By means of recycling the unreacted raw materials could be returned into the process. For consecutive schemes, where the target product is liable to further oxidation, the recycle after separation of such a product allows to increase its yield, due to prevention of the oxidation [4]. The possibility of recycle in the process of NA synthesis was briefly mentioned in [5]. The yield of NA may be increased by 5-6% due to recycling, as mentioned in [6], where it was supposed that the yield of NA increases only due to the drop in the “fresh” βP feed to the reactor [6]. However, the recycling of downstream gas alters the composition of inlet gas and the components ratios in it. This was not taken into account in [5, 6].

In this work, the mathematical modeling of NA synthesis process by βP air oxidation in multi-tubular reactor was carried out, and the factors impacting the process efficiency were studied. Special attention was given to the role of recycle. The analysis was based on a two-dimensional quasi-homogeneous mathematical model of a tubular reactor, which took into account the radial diffusivity and heat conductivity, axial convective mass and heat transfer, radial profile of porosity [7] and was based on a kinetic model of βP oxidation over V_2O_5–TiO_2 ring-shaped catalyst having sizes 4 mm OD, 2 mm ID, and 5 mm length [1].

It was shown that when the portion of the recycling gas increases the portions of the effluent gas and of the fresh air decrease. This results in decrease of O_2/βP ratio (Fig.3). The existing bounds on permissible values of O_2/βP ratio imply bounds on the inlet βP concentration and on the portion of recycle. At the optimally selected parameters of recycling, this provides for substantial increase of S_{NA}, of the overall conversion X and of the yield of NA.

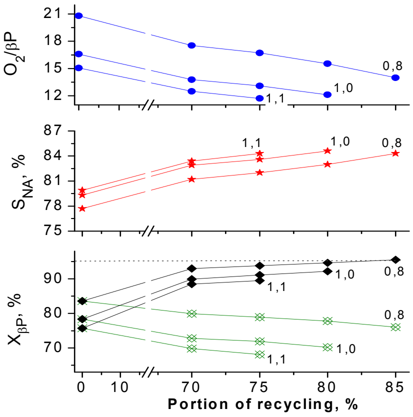


Fig.3. Influence of recycling gas portion on the process parameters. *Inlet concentration of βP (mol.%): 0.8, 1.0 and 1.1*

Optimal regimes were simulated and proposed for technological schemes with and without recycle. The use of recycle after NA separation allows to increase the productivity of the catalyst volume by 13.7%, to increase the yield of NA by 6.7%, to cut the length of tubes by 40%, to decrease the total metal capacity of the tubular section of the reactor by 13.5%, and to decrease the βP consumption per 1 ton of NA by 8.3%.

References

[1]. Ovchinnikova E.V., Andrushkevich T.V., Popova G.Ya., Meshcheryakov V.D., Chumachenko V.A., *Chem. Eng. J.*, V.154, P.60 (2009).

[2]. Andrushkevich T.V., Balzhinimaev B.S., Kashkin V.N., Nakrokhin V.B., Ovchinnikova E.V., Zolotarskii I.A., RU 2371247, (2009).

[3]. Chesalov Yu.A., Ovchinnikova E.V., Chernobay G.B., Popova G.Ya., Andrushkevich T.V., *Catalysis Today*, (2010), in Press, doi:10.1016/j.cattod.2010.01.065.

[4]. Parulekar S.J., Waghmare R.S., Lim H.C., *Chem. Eng. Sci.,* V.43, P.3077 (1988).

[5]. Heinz D., Hoelderich W., Krill S., Boeck W., Hutchmacher K., *CA2281293 (EP-984005),* (2000).

[6]. Andrushkevich T.V., Popova G.Ya., Al'kaeva E.M., Makarenko M.G., Zenkovez G.A., *Chem. Ind.*, №3(165), P.23 (1996) (in Russian).

[7]. Kagyrmanova A.P., Zolotarskii I.A., Vernikovskaya N.V., Smirnov E.I., Kuzmin V.A., Chumakova N.A., *Theor. Found. Chem. Eng.*, V.40, P.155 (2006) (in Russian).

OP-II-9

MULTIPHASE SIMULATION OF A SLURRY BUBBLE COLUMN REACTOR

Donna Post Guillen[1], **Tami Grimmett**[1], **Anastasia M. Gribik**[1] **and Steven P. Antal**[2]

[1]*Idaho National Laboratory Idaho Falls, Idaho, 83415 USA, Donna.Guillen@inl.gov*
[2]*Interphase Dynamics, Glenville, NY 12302 USA, antals@rpi.edu*

The Hybrid Energy Systems Testing (HYTEST) Laboratory is being established at the Idaho National Laboratory to develop and test hybrid energy systems with the principal objective to safeguard U.S. Energy Security by reducing dependence on foreign petroleum. A central component of the HYTEST is the slurry bubble column reactor (SBCR) in which the gas-to-liquid reactions will be performed to synthesize transportation fuels using the Fischer Tropsch (FT) process. SBCRs are cylindrical vessels in which gaseous reactants (for example, synthesis gas or syngas) is sparged into a slurry of liquid reaction products and finely dispersed catalyst particles. The catalyst particles are suspended in the slurry by the rising gas bubbles and serve to promote the chemical reaction that converts syngas to a spectrum of longer chain hydrocarbon products, which can be upgraded to gasoline, diesel or jet fuel.

These SBCRs operate in the churn-turbulent flow regime which is characterized by complex hydrodynamics, coupled with reacting flow chemistry and heat transfer, that effect reactor performance. The purpose of this work is to develop a computational multiphase fluid dynamic (CMFD) model to aid in understanding the physico-chemical processes occurring in the SBCR. Our team is developing a robust methodology to couple reaction kinetics and mass transfer into a four-field model (consisting of the bulk liquid, small bubbles, large bubbles and solid catalyst particles) that includes twelve species: (1) CO reactant, (2) H_2 reactant, (3) hydrocarbon product, and (4) H_2O product in small bubbles, large bubbles, and the bulk fluid. Properties of the hydrocarbon product were specified by vapor liquid equilibrium calculations. The absorption and kinetic models, specifically changes in species concentrations, have been incorporated into the mass continuity equation. The reaction rate is determined based on the macrokinetic model for a cobalt catalyst developed by Yates and Satterfield [1]. The model includes heat generation due to the exothermic chemical reaction, as well as heat removal from a constant temperature heat exchanger. Results of the CMFD simulations (similar to those shown in Figure 1) will be presented.

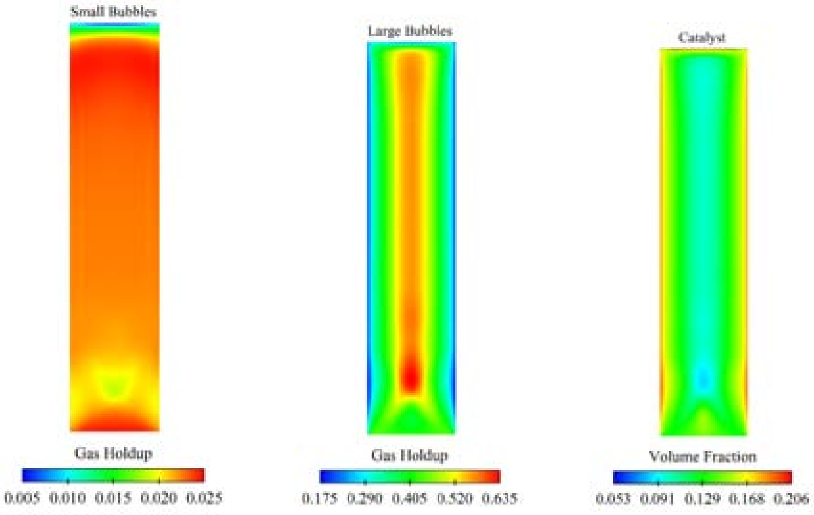


Figure 1. Computed volume fraction of small bubbles, large bubbles and catalyst.

References

[1]. Yates, I.C. and Satterfield, C.N., "Intrinsic Kinetics of the Fischer-Tropsch Synthesis on a Cobalt Catalyst", *Energy & Fuels*, **5**: p. 168-173, (1991)

Acknowledgments

Funding for this research was supported by the U.S. Department of Energy, Office of Nuclear Energy, under DOE Idaho Operations Office Contract DE-AC07-05ID14517.

OP-II-10

NEW OPTIMIZATION-BASED APPROACH TO CHEMICAL REACTOR SYNTHESYS – TOWARDS THE FULL INTEGRATION OF REACTOR DESIGN, OPERATION AND CONTROL

Nikačević N.[1], **Huesman A.**[1], **Van den Hof P.**[1], **Stankiewicz A.**[2]

[1]*Delft Center for Systems and Control, Delft University of Technology,*
Mekelweg 2, 2628 CD Delft, The Netherlands, n.nikacevic@tudelft.nl
[2]*Process & Energy Department, Delft University of Technology,*
Leeghwaterstraat 44, 2628 CA Delft, The Netherlands

Conceptual chemical reactor design still follows traditional procedure which consists of three sequential stages. In the first stage, operation mode is selected according to the particular reaction and manufacturing demands. The decision is strictly based on heuristic rules, for instance batch operation is preferable for small capacities and multi-products while continuous operation is recommended for bulk production of a single product. In the second stage, reactor is designed according to the reaction kinetics and desirable reactant conversion. Although the reaction volume is calculated using mathematical model, this phase also implies the heuristics, as in most cases predefined reactor type is used for a specific application. In the third phase, a control system is designed for the purpose of maintaining the specified product quality and quantity, as well as process safety. This procedure is well established in the practice; it offers ready-made mathematical models and technical solutions. However, it does not provide optimal reactor design from both economical and environmental perspective.

New approach to chemical reactor synthesis is going to be presented and illustrated on an example. The concept is based on dynamic optimization which integrates process design, operation and control. The optimization objectives are primarily economical; though it may include controllability and environmental issues. Optimization results should provide optimal operation mode, optimal process design and optimal control policy. This concept promotes the exploitation of process intensification principles and methods for reactor design. It also explores the possibilities for actuation improvement for the optimal control purposes.

Formulation of unique mathematical model which incorporates all revealed issues is not attainable at the present. Therefore, proposed method implies decomposition of a generic problem into two subproblems to be subjected to an optimization. One model assumes distribution of process variables in space and time; while the other assumes variables' distribution only in time, i.e. lumped in space. Consequently, the first model will generate more spatially-oriented solutions, operated often in continuous regime. The second model will result in more timely-oriented solutions, operated more frequently in discontinues or semi-continuous mode. After dynamic optimizations are performed, the target function values will be compared for a selection of the more beneficial solution.

Reactor synthesis methodology is illustrated on the example of parallel liquid phase reactions – esters saponification reactions for a production of the sterols. The goal is to have a maximum selectivity and yield of the desired sterol product. The reaction rates are slow and consequently long residence times are needed. The narrow residence time distribution is a general recommendation which will be followed here. The precise temperature control is also an objective. According to the approach two models have been set, one which assumes spatial distribution of concentrations and temperature, and the other with lumped process variables. To approach all of the stated goals, process intensification methods will be implemented. In order to meet requirements for long and narrow residence time, oscillatory baffled reactor (OBR) is an effective option for the spatially-oriented solution. For the case of timely-oriented solution, the fed-batch well mixed reactor (FBR) is chosen. Microwave heating is employed for both OBR and FBR, as it provides volumetric heating which can be easily and rapidly actuated for optimal temperature profiles (in space for OBR and in time for FBR). Actuation is additionally intensified by the optimally controlled feeding of the reactant – spatial feeding in OBR and time-varying feeding in FBR. Optimization target function is based on a profit to be maximized – cost of desired sterol produced minus the approximate investment and energy costs. The open-loop controllability study is performed as well, with another target function which defines the process time response to disturbances, to be minimized. For both systems the optimization provides optimal design (volumes, position of feeding points for OBR) and optimal operation procedures (time variation of feed and input heat). The results have been compared to conventional process performed in batch stir tank reactor with external jacket heating. The results demonstrate significant improvements in selectivity and yield of desired product, which is motivating for further development of presented concept.

CATALYTIC DESIGN OF A SINGLE CHANNEL MONOLITH FOR THE PARTIAL OXIDATION OF METHANE TO SYNTHESIS GAS

Gubanova E.[1], **van Veen A.C.**[2], **Sadykov V.**[1,3], **Mirodatos C.**[4], **Mezentseva N.**[1]

[1]Boreskov Institute of Catalysis SB RAS, pr. Lavrentieva, 5, Novosibirsk, 630090, Russia, gubanova@catalysis.ru
[2]Ruhr-University Bochum, Lehrstuhl für Technische Chemie, Office NBCF 04/685, Universitätsstraße 150, D-44801 Bochum, Germany
[3]Novosibirsk State University, Pirogova 2, Novosibirsk, 630090, Russia
[4]Institut de Recherches sur la Catalyse et l'Environnement de Lyon, F-69626 Villeurbanne Cedex, France

Structured reactors are progressively acquiring an important role in chemical industry and environmentally benign technology, such as the monolithic automotive exhaust catalysis. Efficient mass and heat transfer among phases at low pressure drop is the underlying reason for the attractively of these systems. Beyond that catalyst development for demanding and difficult to control reactions, like partial oxidations at high temperatures, also benefit strongly from these features. This holds especially for channel systems with coated catalysts allowing studies on a larger variety of catalytic materials than systems with uniform grid, woven, foam or foil catalysts previously employed [1,2]. The possibility of implementing a concept for the effective distribution of the active component along monolith channels presented in this paper is another major advantage of using catalytic coatings. The present case study investigates the catalytic partial oxidation of methane (CPOM).

Dispersed complex oxides $Pr_{0.3}Ce_{0.35}Zr_{0.35}O_x$ were prepared via the Pechini route [3,4] and supported on the walls of separate triangular channels of α-Al_2O_3 monolith (wall thickness 0.2 mm, triangle side 2.33 mm, channel length 20 mm) from a water suspension ultrasonically dispersed under addition of peptizers and surfactants (loading up to 10 wt.%). Pt (1.4 wt.%) was supported by incipient wetness impregnation with H_2PtC_6 solution. Catalytic experiments were carried out using quartz reactors and flow installations equipped with an Agilent Micro-GC 300. The CH_4 concentration in the feed was 7% at a CH_4:O_2 ratio = 2, the temperature range was 650 – 800°C and studied contact times were 1 - 28 ms. Before reaction, samples were pretreated at 700°C in an diluted oxygen stream.

Steady-state experiments revealed that Pt is required for the steam/dry reforming activity of the catalyst, since it has been shown that the reforming on the Pt-free support is inefficient. On the other hand, despite the beneficial action of the mixed oxide support, it comes that the presence of Pt in the inlet zone of the catalyst, where high oxygen partial pressures still exist, leads to an over-oxidation of the desired products CO and H_2. Based on the received data a new structured catalyst concept is proposed with a very low Pt concentration at the monolith inlet and successive increase along the flow direction. The intrinsic activity of the mixed oxide is exploited for the syngas formation at the monolith inlet with extensive presence of oxygen, while in the downstream section, once oxygen concentration is lowered, the rising Pt content in the catalyst favors at low oxygen pressure both the direct partial oxidation and the dry/steam reforming of remaining methane. The concept also results in a favorable heat management and reactor size, since the initial catalyst section without Pt and lower catalyst activity is only slightly overheated, while the reforming section with Pt can be shortened, as smaller quantities of CO_2 and H_2O require reforming. On the basis of the presented concept, a new combination of active components supported on the single corundum monolith channel was prepared with Pt added to the doped mixed oxide only partially, i.e. in the downstream segment. This new catalyst was tested and compared to a system with homogeneous Pt concentration in the monolith coating under the same CPOM conditions. Stability test with fresh catalysts revealed that channels without Pt in the inlet section stabilize much more rapidly than Pt gradient-free systems. Even after 26h on stream this latter system did not reach steady state operation. It should be stressed, that yields of synthesis gas for system with Pt gradient in the inlet part were higher then those for other system with homogeneous Pt distribution, i.e. overall larger quantity of supported Pt.

In summary, the present work outlined a new concept for the effective distribution of the active component along single a channel monolith successfully tested for its use in catalytic partial oxidation of methane.

References

[1]. C.R.H. de Smet, M.H.J.M. de Croon, R.J. Berger, G.B. Marin, et al., AIChE J. **2000**, 46, 1837-1849.
[2]. D.A. Hickman, L.D. Schmidt, AIChE J. **1993**, 39, 1164-1177.
[3]. V. Sadykov, S. Pavlova, et al., Kinetics and Catalysis **2005**, 46, 227-250.
[4]. T.G. Kuznetsova, V.A. Sadykov, et al., Stud. Surf. Sci. Catal. **2002**, 143, 659-667.

Acknowledgements

This work was carried out in frames of Russian-French Associated European laboratory on catalysis and supported by RFBR–CNRS 09-03-93112 Project.

OP-II-12

EVALUATION OF IT-SOFC REACTOR FOR METHANE PARTIAL OXIDATION WITH TEMPERATURE PROGRAMMING METHODS

Tomohiko Tagawa[1], Yusuke Yoshida[1], Hiroshi Yamada[1], Makoto Inomata[2]

[1]*Department of Chemical Engineering, Nagoya University Japan, Nagoya, Japan*
tagawa@nuce.nagoya-u.ac.jp
[2]*AJGC corporation, Japan*

Introduction

Highly selective oxidation processes of methane are urgently required. Fuel cell system using solid oxide electrolyte attracts considerable attentions as a membrane reactor for selective oxidation reactions. The molecular selective permeability of oxygen anion through the solid oxide electrolyte membrane can reduce the oxygen production plant and can give high selectivity. This system can also convert the excess heat of reaction into electricity, as is called a "Chemicals-Energy co-generation"[1]. Applied potential operation is also of recent interest [2]. For the highly selective oxidation system, design and preparation of anode catalyst are essential [3,4]. A mist pyrolysis method is an effective method for preparation of fine anode particles on the surface of YSZ (Yttria Stabilized Zirconia) electrolyte [4,5]. As the operation temperature of YSZ (= about 1300K) is much higher than the reaction temperature of partial oxidation of methane, we have studied partial oxidation of methane with intermediate temperature solid oxide fuel cell (=IT-SOFC) system using $LaGaO_3$ type electrolyte (=LSGM)[6]. In this study, permeation of oxygen through the IT-SOFC reactor was evaluated by means of temperature programming method.

Experimental

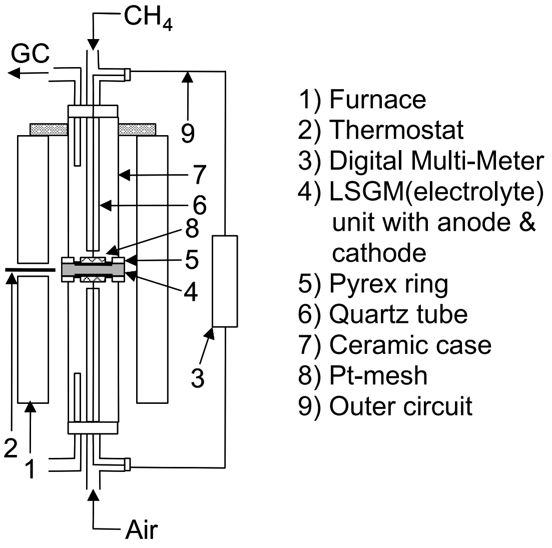


Fig. 1. Experimental set up

Figure 1 shows the schematic view of reaction apparatus. Two ceramic tube chambers were divided by $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_3$ (φ : 42 mm, t : 0.3 mm) type electrolyte(LSGM). Fused Pyrex rings placed at the both side of electrolyte were used as a gas seal. On the both side of the electrolyte surface, an anode catalyst ($Ni\text{-}Li/Al_2O_3$) and a cathode catalyst ($La_{0.6}Sr_{0.4}CoO_3$ = LSC) were prepared. Platinum mesh and platinum wire were used to connect to current meter. He (3.02×10^{-5} mol/s) was fed into the anode side and the outlet was connected to G.C. *via* sampling valve. Oxygen (1.58×10^{-5} mol/s) was fed into cathode side.

Results and Discussion

Figure 2 shows the partial oxidation of methane with IT-SOFC reactor. Conversion increased above 1000K. Figure 3 shows the oxygen TPD spectra of NiLi/Al_2O_3 anode under various rate of temperature increase. Desorption of oxygen with activation energy higher than 240 kJ/mol was observed above 800K. Figure 4 shows TPD spectra of LSGM electrolyte powder. Desorption of oxygen with activation energy of 240 kJ/mol was observed above 800K. Figure 5 shows the permeation of oxygen from fuel cell unit. Permeation rate was increased above 1000K showing that active oxygen observed in Figs. 3 and 4 might permeate through the unit. This behaviour agrees with methane oxidation activity shown in Fig. 2. These results indicate that temperature programming method is useful to elucidate the behaviour of active oxygen species.

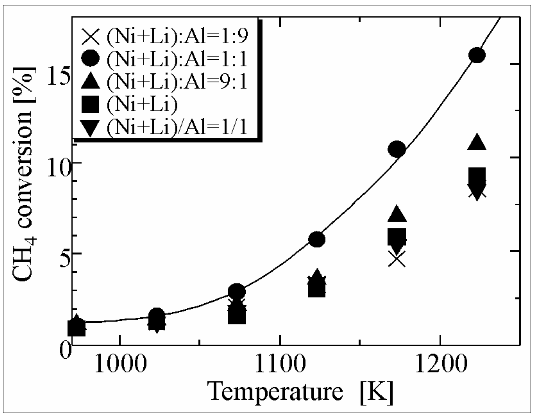


Fig. 2. Methane oxidation with SOFC reactor

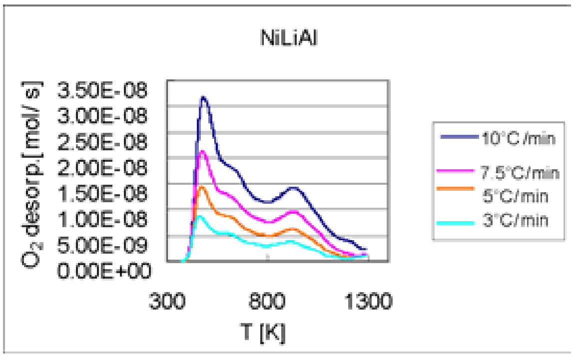


Fig. 3. TPD of NiLiAlO anode catalyst

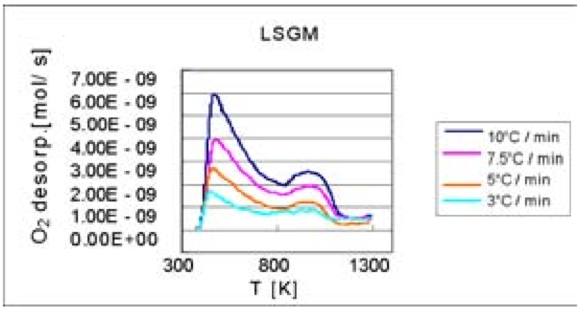


Fig. 4. TPD of LSGM powder

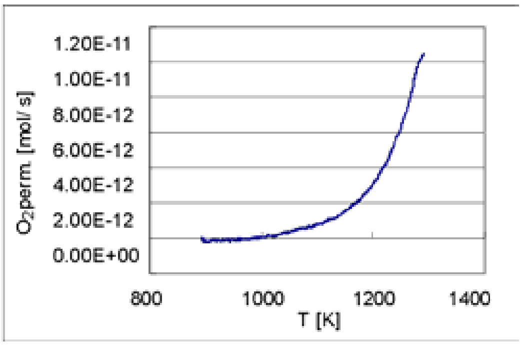


Fig. 5. TPD of NiLiAlO/LSGM/LSC unit

References

[1] T. Tagawa, et Al., *Chem. Eng. Sci.*, **(1999)** 54, 1553.
[2] T. Tagawa, et al., *Chem. Eng. Journal*, **(2003)** 93,3.
[3] T. Tagawa, et al., *Solid State Ionics*, **(1998)** 106, 227).
[4] K. K. Moe, et. Al., *J. Ceram. Soc. Japan*, **(1998)** 106,754.
[5] A. Carrillo, T. Tagawa and S. Goto, *Mat. Res. Bull.*, **(2001)** 36,1017.
[6] M. Ito, T. Tagawa and S. Goto, *J. Japan Petro. Inst.*, **(2001)** 44,371.
[7] T. Tagawa, et al., Proc.ICIM-9, **(2006)**, 579.

Acknowledgements

The authors are grateful to Japan Fine Ceramics Co. for providing LSGM membrane and to Mr. Hajime Itoh of Nagoya University for his technical assistance.

OP-II-13

HYDROGEN PEROXIDE DIRECT SYNTHESIS IN A TRICKLE BED REACTOR: THE ISSUE OF SELECTIVITY

Pierdomenico Biasi[1], Federica Menegazzo[2], Francesco Pinna[2], Kari Eränen[1], Paolo Canu[3], Tapio Salmi[1]

[1] Process chemistry centre (PCC), Laboratory of Industrial Chemistry and Reaction Engineering Åbo Akademi, Biskopsgatan 8, TURKU 20500 FINLAND,
E-mail: bpierdom@abo.fi
[2]Dipartimento di Chimica, Università di Venezia, and Consorzio INSTM, 30123 Venezia, Italy
[3]Dipartimento di Principi e Impianti di Ingegneria Chimica "I. Sorgato" (DIPIC) University of Padova, via Marzolo 9, 35131, PADOVA, Italy

Hydrogen peroxide has always been considered a very interesting and environmentally friendly oxidant with applications confined mainly in unselective sectors such as the paper and textile industries and the treatment of waste waters. The direct synthesis attracted renewed interest after 1980 due to the increased demand of H_2O_2 as a green oxidant. It could soon compete with the indirect process if selectivity based on H_2 can be sufficiently high. The direct H_2 oxidation process has been extensively investigated, leading to a large number of publications in the last few years [1]. Recently, Basse and Jaeger [2] reported that a demonstration plant is ready to enter production. Research in the H_2O_2 direct synthesis so far mostly focused on the identification and development of the catalyst. The present work is based on earlier work of Strukul and coworkers [3], who synthesized several promising catalysts mono- and bimetallic catalysts. We are currently investigating opportunities of engineering the reaction, based on one of those good catalysts, rising the scale of investigation, implementing continuous operation. We illustrate how a trickle bed reactor allows to combine gas and liquid residence time to achieved enhancements of selectivity, up to 90%, for a catalyst based on PdAu-ZS.

Catalityc tests were conducted in a trickle bed reactor at 10 bar and -10°C.

The overall length of the reactor is 280 mm and the internal diameter 11.5 mm. The gas reagents (O_2/H_2) were fed in the reactor with 2 mass flow controllers, as mixtures with CO_2. Methanol was used as liquid solvent and then reaction medium and it was fed with a syringe pump. Sulfated zirconia-supported catalysts, Pd-ZS [3] was the catalyst chosen for the reaction. It was diluited with silica (1:1 in weight), and the particles size of inert and catalyst was between 0.5 and 1 mm. The length of the catalyst bed was 6 mm. Three different liquid flow rates and seven different gas flow rates were investigated to perform the reaction in the trickle flow regime.

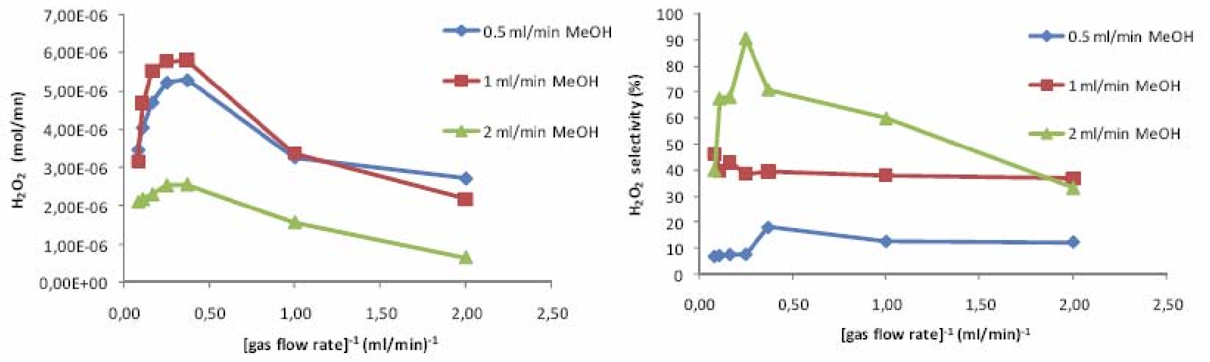


Fig. 1. Production rate (left) and selectivity (right) of hydrogen peroxide at -10°C and 10 bar, gas composition in the inlet $CO_2/O_2/H_2$ respectively 80%/16%/4%.

Results are shown in Fig. 1 (left). Experiments carried out by feeding the methanol at 1 ml/min and the gas between 0.11 and 0.37 min/ml behave differently with respect to the case a larger liquid flow rate (2 ml/min) and the same gas flow. At a lower liquid flow rate, i.e. larger liquid residence time, the productivity (moles of H_2O_2 /min) is larger, as expected. On the other hand, gas flow rate affects productivity non-linearly, passing through a maximum. Note that a larger H_2O_2 flow rate at the lower liquid flow rate imply a gain in concentration. It also confirms the opportunities of affecting the reaction course in a TBR by suitably combining vapour-liquid equilibrium, interphase mass-transfer, and catalyst surface renewal. The major concern in direct synthesis is poor selectivity because of the complex reaction network, involving product degradation steps and by-products (H_2O). The assumption is that independent manipulation of gas and liquid contact time, as well as the concentrations of the gases, provides opportunities to control the reaction path through its mechanism. Fig. 1 (right) shows how contact time between catalyst and liquid-gas components can affect the selectivity. The results achieved are about two times higher than in the reactor used to develop and test the catalyst [3], which was operated by continuously flowing gas through the liquid and solid, well stirred, batch suspension. The full results with other catalysts are presented in the full manuscript.

References

[1]. Samanta, C. Direct synthesis of hydrogen peroxide from hydrogen and oxygen: An overview of recent developments in the process. Applied Catalysis A: General. 2008, 350, 2, 133-149.

[2]. Basse, C.; Jaewger, B.; Elem.-Degussa Sci-Newsletter, 2008, 17, 4.

[3]. Menegazzo, F.; Burti P.; Signoretto, M.; Manzoli, M.; Vankova, S.; Boccuzzi, F.; Pinna, F.; Strukul, G. Effect of the addition of Au in zirconia and ceria supported Pd catalysts for the direct synthesis of hydrogen peroxide. Journal of Catalysis. 2008, 257, 2, 369-38.

OPTIMIZED OPERATING STRATEGY FOR INDUSTRIAL ETHYLENE OXIDE REACTOR

Gomes V.G.[1] **and Ngian K.**[2]

[1]*School of Chemical and Biomolecular Engineering, University of Sydney,*
NSW 2006, Australia, *vincent.gomes@sydney.edu.au*
[2]*Huntsman Corporation Australia, Botany Rd, Sydney, Australia*

INTRODUCTION

This work is focused on evaluating the effects of catalyst promoter and process variables for selective oxidation of ethylene to ethylene oxide in an industrial fixed-bed reactor. The multiple chemical reactions involved in the synthesis of ethylene oxide are highly exothermic, thereby making reactor conversion, selectivity and temperature control for the unit rather challenging. The objective is to identify and test the critical variables to maximize the productivity of ethylene oxide product in an existing full-scale production facility without compromising personnel safety, plant hazard and equipment integrity. Our analysis was conducted by applying dynamic simulation models to investigate and optimize the performance of the reactor.

MODELLING

We developed the governing dynamic models of the reactor with the inclusion of multiple reactions by deriving the species balances for the catalytic process under non-isothermal conditions. The kinetic parameters for the model were obtained from literature data for our catalyst [1-3]. The sets of nonlinear kinetic rates of the epoxidation of ethylene (and other side reactions that affect the process) to ethylene oxide over the silver catalyst are strongly coupled with heat and mass transport, and the governing equations. The model incorporates both catalyst deactivation and the effect of the promoter or moderating agent: 1,2-dichloroethene (DCE). The model predictions were validated against plant data obtained from an operating industrial ethylene oxide reactor over the plant operating period of three years.

RESULTS AND DISCUSSIONS

Our model predictions were found to compare well with experimental data. The model was subsequently used to analyse process sensitivity and optimization of the operating conditions. The catalyst temperature was found to have major effects on the reactor performance, catalyst aging and plant safety. The inlet temperature of oil as coolant is an important control variable which could regulate possible thermal runaways as well as the reactor performance. However, we found that there are limitations on the allowable temperature rise of the coolant as it passes through the reactor. On one hand, it is advantageous for the temperature to rise enough to allow efficient heat transfer in the secondary heat exchanger (dissipated via steam generation), however is also strong motivation to minimize the temperature rise in order to reduce thermal shocks to the reactor.

REFERENCES

[1]. Petrov, L. Eliyas, A. and Shopov, D, 'A Kinetics of Steady State Ethylene Epoxidation over a Supported Silver Catalyst‴, *Applied Catalysis*, vol 18, pp. 87-103, **1984**.

[2]. Borman, P.C. Westerterp, K.R, 'An experimental study of the kinetics of the selective oxidation of ethene over a silver on α- alumina catalyst', *Ind. Eng. Chem. Res*. Vol 34,pp. 49–58, **1995**.

[3]. Boskovic, G. Dropka, N. Wolf, D. Brückner, A. and Baerns, M, , 'Deactivation Kinetics of Ag/Al_2O_3 Catalyst for ethylene Epoxidation', *Journal of Catalysis*, vol 226, pp. 334, **2004**.

OP-II-15

DEVELOPMENT OF A REACTIVE DISTILLATION PROCESS FOR ACETAL PRODUCTION: EXPERIMENTAL STUDY AND SIMULATION MODEL

Agirre I., Barrio V.L., Güemez B., Cambra J.F., Arias P.L.

Escuela Técnica Superior de Ingeniería de Bilbao. Alameda Urquijo s/n 48013 Bilbao (Bizkaia), Spain. ion.agirre@ehu.es

Nowadays, the use of biofuels in conventional car engines has become one of the technological goals towards a sustainable development and oxygenated compounds like acetals seem to be good candidates to enhance cetane number of biodiesels. [1]. In this paper, an acetalization reaction, which consists on the reaction between butanal and ethanol will be considered. The main reaction implies the production of the corresponding acetal (1,1 diethoxy butane) and water. This reaction presents high thermodynamic limitations and using conventional reaction systems the achieved conversions are around 40% [2]. In order to overcome these limitations, an innovative reaction system like catalytic reactive distillation is required. Due to the distillation effect, the reaction products are being removed from the reacting mixture and higher conversions can be achieved.

The experimental work carried out in a semi pilot reactive distillation plant will be presented. Katapak SP-11 modules with Amberlyst 47 ion exchange resins were used as catalytic structured packing. The effect of different parameters was studied: effect of the reaction section height, effect of the reflux ratio, different feeding configurations. All these experiments allowed finding the best column configuration for optimum performance.

One of the main conclusions reached is that working at high reflux ratios equilibrium conversions can be overcome but a low acetal concentration in the reboiler is produced. On the other hand, working at low reflux ratios, lower conversions were achieved but the acetal concentration in the reboiler was around 80% in mol (see Fig. 1). In this last case, a side reaction was observed due to the required high temperatures in the reboiler. Small amounts of 1,1-diethoxy butane is converted into 1-ethoxy-1-butene and water;. Another interesting conclusion is that higher conversions are achieved if the reactants are fed to the system from a unique point, the top side of the reactive section. It seems that the volatility difference between ethanol and n-butanal is not high enough to justify feeding them separately.

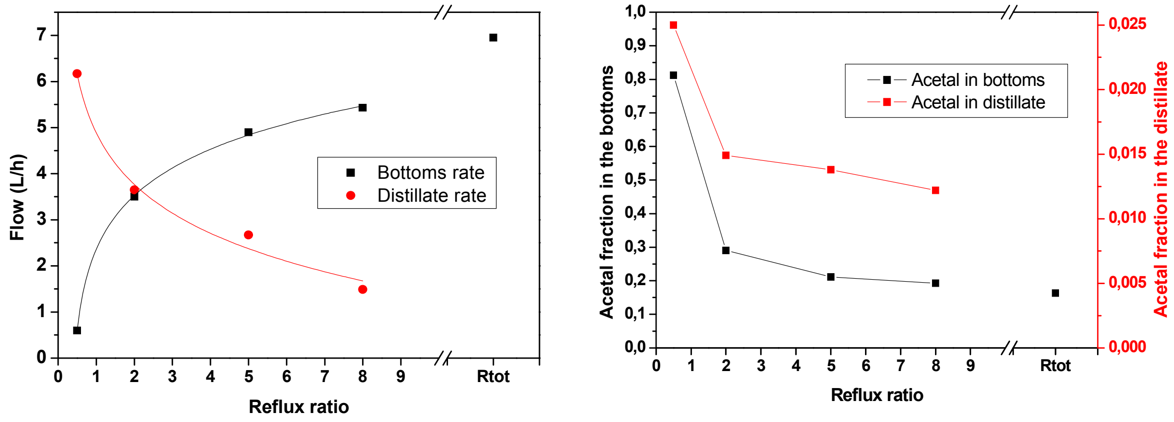


Figure 1: Volumetric flow rate and acetal concentration in the outputs.
5 Katapak SP-11 modules.

Once the experimental work was finished, a steady state reactive distillation model based on conventional MESH equations was developed in order to gain further insights and to predict results without carrying out additional experiments. Every stage was considered adiabatic and non-ideal liquid mixture behaviour was considered (NRTL model was chosen as the most suitable one [3]). A total condenser was supposed and the possibility of two different feed points was taken into account. First of all, the model was validated with experimental data and afterwards several column configurations were tested in order to find the most appropriate one. One interesting conclusion is that the model explains how the reverse reaction can influence when catalytic section is too high. The model is also able to simulate the change from direct to forward reaction in the lowest part of the reacting section due to the high acetal concentrations (above the equilibrium ones) that come from the catalytic upper part.

References

[1]. M.R. Capeletti, L. Balzano, et all. *Appl. Catal.* **(2000)** 198 L1-L4
[2]. I. Agirre, V.L. Barrio, B. Güemez, J.F. Cambra. and P.L. Arias., *IJCRE.* (To be published)
[3]. T.M. Letcher, G.G. Redhi, S.E. Radloff, U. Domanska, *J. Chem. Eng. Data (***1996), *41,* 707-712**.**

Acknowledgements

The authors gratefully acknowledge the financial support by the Spanish Ministry of Science and Technology (ENE2006-15116-C04-03/CON), the Basque Government (IE06-171) and the University of the Basque Country (UPV/EHU). Besides, the authors want to mention the collaboration of Rohm & Haas for kindly supplying different Ambestlyst resins.

OP-II-16

MYTHOLOGY IN MULTIPHASE CATALYSIS: WHY DO THE CONVENTIONAL FIXED-BED TECHNOLOGIES HAVE NO POTENTIAL FOR THE FURTHER PROCESS DEVELOPMENT?

Leonid B. Datsevich[1,2]

[1]The University of Bayreuth (Germany)
[2]MPCP GmbH (Bayreuth, Germany)
E-mail: datsevich@mpcp.de, datsevich@uni-bayreuth.de

The conventional multiphase fixed-bed (trickle-bed and bubble (packed) column) reactors are very often designated for exothermic reactions, for example, such as hydrogenation, hydrotreating, purification, the Fischer-Tropsch synthesis, etc.

The contribution deals with the analysis of these reactors with regard to process efficiency, safety and design.

The paper shows that these reactors do not possess any potential for development. Any attempt to improve substantially the reactor performance, e.g. to enhance the reactor productivity (not by several percent as it is always discussed in the available literature, but by several times) cannot be realized because of the restrictions imposed by the process arrangements.

The paper retraces the original ideas developed by the previous generation of the process developers and indicates how these ideas became the rigid paradigm that hindered the progress in the process development.

The old mythology deeply established in the scientific and industrial communities is discussed in light of modern concepts in mass transfer and kinetics.

The contribution disproves the following typical myths in the process design of multiphase fixed-bed reactors with a gas loop:

(1) Operating pressure has to be high in order to increase the concentration of the gaseous compound in the liquid phase and, consequently, the reactor productivity.

(2) The reaction rate is limited by mass transfer of the gaseous compound and, therefore, operating pressure has to be high in order to enhance gas-liquid-solid mass transfer.

(3) The high concentration of the liquid compound at the reactor inlet and high operating pressure have to influence the reactor productivity nearly proportionally to these factors if the reaction rate has the first order with respect to both gas and liquid reactants.

(4) The gas recirculation rate has to be high for providing the greater gas concentration on the catalyst surface (for speeding up the reaction rate or slowing down the catalyst aging).

(5) The gas recirculation rate has to be high for decreasing the content of by-gases in the loop (e.g. hydrogen sulfide in hydrotreaters).

(6) High pressure in the reactor unconditionally encourages the slower catalyst deactivation.

Some approaches towards the new process embodiments are also presented.

CATALYTIC COATING OF METALLIC SUBSTRATES AND APPLICATIONS TO INSERTS AND CATALYTIC REACTORS

Löfberg A.[1], Essakhi A.[1], Swesi Y.[2], Meille V.[2], Pitault I.[2], Paul S.[1], Supiot P.[3], Mutel B.[3], Le Courtois V.[1], Bordes-Richard E.[1]

[1]*Unite de Catalyse et de Chimie du Solide, UMR CNRS 8181, Universite Lille 1, Villeneuve d'Ascq, France, Axel.Lofberg@univ-lille1.fr*

[2]*Laboratoire de genie des procedes Catalytiques, UMR CNRS 2214, CPE-Lyon, Villeurbanne, France*

[3]*IEMN -UMR CNRS 8520, Universite Lille 1, Villeneuve d'Ascq, France*

Catalytic micro(milli)reactors or structured reactors offer a potential to conduct mass or heat transfer-demanding reactions under safe conditions while maintaining and/or increasing selectivity and productivity. Whatever the size and the design of the reactor the key material is the catalytic active phase which must be deposited as thin layers onto the metallic inserts or reactor walls of reactor. This assembly must be mechanically and thermally stable, and chemically resistant. Moreover the active phase must retain its own surface area, porosity, and activity, selectivity.

We have investigated the parameters leading to successful coating by oxides that bear no chemical resemblance with the metallic substrate. Stainless steel (SS) or FeCrAlloy 5×2×0.05 (mm) plates (to figure out reactor walls) and foams (Porvair®, various ppi) as inserts were used as substrates. Two model reactions were studied. One was the oxidative dehydrogenation of propane on 7%VO_x supported on TiO_2 [1], the other was the dehydrogenation of methylcyclohexane (MCH) on a supported metal, 2%Pt/Al_2O_3 [2]. Several methods of coating were used after cleaning and appropriate pretreatments of plates/foams, from dip-coating in suspension with control of the rheology for TiO_2 and alumina supports [3], to grafting by alcoolates (VO_x polyvanadates) or impregnation (H_2PtCl_6) followed by calcination or *in situ* heat treatment, respectively, to get the active phase. In a former work on 7%VO_x/TiO_2/SS plates, Fe was shown to diffuse outwards and to poison vanadium leading to decrease of the selectivity to propene in the ODH of propane [1]. To avoid that, a primer consisting of a micron-thick silica-like layer intended to act as a barrier was deposited onto the metal by RPECVD (Remote Plasma Enhanced Chemical Vapor Deposition). This method was successful for coating cobalt on silica support onto stainless-steel plates for Fisher-Tropsch reaction [4]. The technology was adapted to the coating of foams by using a specially designed sample holder [5]. Figure 1 shows the layers of TiO_2/SiO_2 on a branch of foam and on the surface of a plate analysed by Electron Probe Micro Analysis.

Catalytic reactions were carried out in specially designed reactors, and the catalytic properties were compared with those of powders (7%VO_x/TiO_2) or of coated beads (Pt/Al_2O_3). In the latter case for example the hot spot temperature and MCH conversion were studied for three foams differing by the material (FeCrAlloy or α-alumina), ppi and porosity, and compared to coated beads (Table 1). Ca. 2.6 g of Pt/Al_2O_3 was coating foam insert or beads displayed in a 19 cm-long house-designed reactor. In all cases the hot spot was higher for beads while the conversion trend is less easy to see. Therefore even for highly exothermic reactions not limited by external transport, coated foams significantly increase the effective conductivity of catalytic beds, the higher foam density leading to a higher effective conductivity.

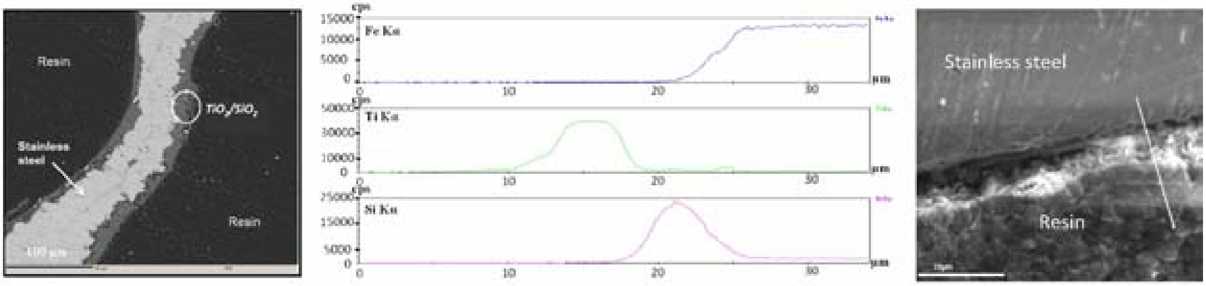


Figure 1. Electron Probe Micro Analysis of a branch of stainless steel foam (left) and plate (right) coated by TiO_2/SiO_2 after RPECVD, and profiles of Fe, Ti, Si (middle) along the white arrow (right).

Table 1. Hot spot (ΔT) and MCH conversion (X) for three foams and for zeolithic beads.

W/F_{MCH} ($kg_{cata}.s.mol^{-1}$)	F1 : Metallic 33 ppi*, $\varepsilon^{\#}$ = 97%		F2 : Metallic 33 ppi, ε = 81%		F3 : Ceramic 37 ppi, ε = 87%		Molecular sieves Bead ∅ 2 mm	
	ΔT°C	X (%)	ΔT°C	X (%)	ΔT°C	X (%)	ΔT°C	X (%)
15.3	36	97	8	95	12	77	35	96
30.6	40	88	11	87	19	74	49	91

* ppi: pound per square inch; #ε: porosity; $Q_{H2} = 3.3\cdot10^{-4} mol.s^{-1}$; T°controller 300°C.

References

[1]. T. Giornelli, A. Lofberg, E. Bordes-Richard, Appl. Catal. A : General, **2006**, 305, 197-203.

[2]. M. Roumanie, V. Meille, C. Pijolat, G. Tournier, C. de Bellefon, P. Pouteau, C. Delattre, Catal. Today **2005**, 110, 164-170.

[3]. V. Meille, Appl. Catal. A: General **2006**, 315, 1-17.

[4]. T. Giornelli, A. Lofberg, L. Guillou, S. Paul, V. Le Courtois, E. Bordes-Richard, Catal. Today, **2007**, 128, 201-207.

[5]. A. Essakhi et al.A. Lofberg, P. Supiot, B. Mutel, S. Paul, V. Le Courtois, E. Bordes-Richard, Proc. 6th Int. Symp. Polyimides and Other High Temperature/High Performance Polymers, Melbourne, Florida, USA, November 9-11, **2009**. Accepted.

Acknowledgements

The Agence nationale pour la Recherche is acknowleged for A. Essakhi's grant and financial support.

PERFORMANCE OF SELECTIVE OXIDATION REACTIONS IN FLUIDIZED BED REACTOR: GAS INTERPHASE TRANSFER AND CATALYST UNSTEADY STATE

Pokrovskaya S.A.

Boreskov Institute of Catalysis SB RAS, 630090, pr. Lavrentieva 5, Novosibirsk, Russia, pokrov@catalysis.ru
Novosibirsk State University, 630090, Pirogova 2, Novosibirsk, Russia

Catalytic reactors with fluidized bed are an attractive alternative for exothermic heterogeneous processes of selective oxidation as compared with fixed bed reactors because of favourable rates of heat transfer providing temperature uniformity, absence of pore-diffusion limitation and others. However, the decrease of desired product selectivity is observed in a number of cases, that restrains a wide application of fluidized bed reactors for such processes. The latest comprehensive reviews of studies of catalytic systems with fluidized bed show that the major part of research dealing with selectivity improvement is referred to hydrodynamic aspects, mainly to the increase of gas-solid contact by modifications in design such as turbulent fluidization. A lot of mathematical models based on the assumption of steady state kinetics are elaborated to study hydrodynamic effects in these systems [1, 2].

At the same time, a number of studies indicated that the unsteady state of catalyst surface leads to the difference of product selectivity and may provide its significant enhancement [3-8]. This work aims to elucidate comparative effect of gas interphase transfer (GIT) and unsteady catalyst state on selectivity in the reactor with turbulent fluidized bed. The mathematical description on the base of dynamic kinetic model used for present studies was given in other studies [3]. Modeling was performed with model kinetic scheme and catalyst state in the processes of selective o-xylene oxidation and propylene ammoxidation was analyzed.

At first, the reaction scheme with three catalytic steps was used: a) $B + [\ ] \rightarrow [B]$, b) $A + \nu_1[B] \rightarrow C + \nu_1[\ ]$, c) $C + \nu_2[B] \rightarrow D + \nu_2[\ ]$, where A – the reagent, B – the oxidant (oxygen), C – the desired product, D – the undesired product. Computational runs were fulfilled at isothermal regime with contact time of 2-7 s^{-1} for three cases:

Case	1	2	3
Surface coverage	steady	steady	unsteady
GIT coefficient, s^{-1}	∞	0,5-2	0,5-2

At steady surface coverage by oxidized forms [B], GIT impact (Case 2) results in 2–5% selectivity decrease compared to plug flow reactor (Case 1) for the conditions under study. The analysis of the dense phase profiles of the reagent concentrations and the catalyst surface coverage has shown that for Case 3 selectivity difference is varied with contact time, reaction rate parameters, and input reagent concentrations. In a number of cases the selectivity decreased by 3-7% compared to Case 2, thus summarized decrease achieves 7-10%. But the formation of unsteady surface state with higher selectivity by operation conditions allows not only to level the negative GIT effect but also to reach the selectivity higher than in Case 1 by 4-6%.

The results obtained were verified simulating the processes of o-xylene oxidation to phthalic anhydride (PA) and propylene ammoxidation to acrylonitrile on the base of dynamic kinetic model. Three cases given above are considered also. For o-xylene oxidation over V-Ti-O catalyst, the PA yield in the fixed bed at plug flow regime is equal to 81% (Case 1) and 76-78% for Case 2. It is revealed that the higher is the o-xylene concentration the greater is the surface coverage reactive species that are converted to PA, and the lower is the oxidized state, the higher is the selectivity. The formation of unsteady surface state by special operation conditions increases PA yield up to 88-90%. The modeling results are confirmed by experimental data [5]. Similar results for propylene ammoxidation to acrylonitrile on 8-component catalyst show that the acrylonitrile yield is about 77% for Case 1, 72-74% for Case 2, and 80% for Case 3.

Thus, the unsteady state of catalyst surface as well as gas transfer between the dense and bubble phases could be considered as key factors that determine the product selectivity of oxidation processes in the reactors with turbulent fluidized bed.

References

[1]. H.T.Bi, N.Ellis, I.A.Abba, J.R.Grace, CES, **2000**, 55, 4789-4825.

[2]. A. Mahecha-Botero, J.R. Grace, S.S.E.H. Elnashaie, C. Jim Lim, 2009, Chem. Eng. Comm., **2009**, 196, 1375–1405.

[3]. M.G. Slinko., S.A. Pokrovskaya, V.S. Sheplev, Dokl. AN SSSR, **1979**, 244, 669-673.

[4]. A.N. Zagoruiko, CEJ, **2005,** 107, 133-139.

[5]. A.A. Ivanov and B.S. Balzhinimaev, In Proceedings of the International Conference "Unsteady State Processes in Catalysis", Utrecht, The Netherlands, Tokyo, Japan: VSP, **1990**, 91-113.

[6]. D. Bulushev, E. Ivanov, S. Reshetnikov, L. Kiwi-Minsker, A. Renken, CEJ, 2005, 107, 147-155.

[7]. G.A. Bunimovich, P.L. Silveston, Y.S. Matros, In Handbook of Heterogeneous Catalysis, Germany, Wiley-VCH, **2008**, 2156-2173.

[8]. S.A. Pokrovskaya, M.G. Slinko, In Proceedings of XVII International Conference on Chemical Reactors, Greece, **2006,** 175-179.

DESIGN AND OPERATION OF COMPUTER-CONTROLLED PULSED MULTIJET LIQUID FEED FOR HEAT-TRANSFER DEVICE

Simakov V.[1,2], Bodrov M.[1], Nazarov A.[1], Serov A.[1]

[1]Institute of Thermophysics SB RAS, Novosibirsk, Russia, sova3d@mail.ru
[2]Novosibirsk State University, Novosibirsk, Russia

Pulse liquid feeds are often introduced into gas-solid systems through horizontal nozzles in many industry applications including chemical reactor engineering. The interactions of gas, particles and pulse spray play key roles in affecting process efficiency and product quality [1]. Good understanding of the fundamental hydrodynamics and heat transfer of this phenomenon is essential to the design improvement and optimization of chemical process.

In the present work a pulsed source of gas-droplet multijets with control system supplied by computational soft program, sensors and apparatus for experimental pilot set up were developed to study heat transfer between water spray and heat exchanger. To provide on-line experimental study of a heat transfer between liquid jets and heating surface it was synchronized both detecting the numerous measuring parameters for every nozzle (time of liquid valve opening, pulse frequency, registration of two-phase jet towards vertical and horizontal axes, hydraulic pressure drop and etc.) and their quick proper computation to obtain comprehensive analysis. The methods of registration, instrumentation and processing techniques for unsteady-state flow regime were also developed in this study and described in details. During heat-transfer experiment a special attention was paid to reduce a parameter's measurement time that includes time for system relaxation after the changing experimental regime and time for registration of proper parameter response. The process of measurement is continuous to identify the end of a transient period and the beginning of the operating mode.

Experimental set-up (Fig. 1) consists of the next main units [2, 3]: special digital calorimeter device connected with a heat-exchanger surface (1), programmable source of multijet feed (2), and computerized registration system. During the generation of impulse jets the main parameters of water-droplet and air flows were measured as well as dynamic of liquid and gas spreading on the

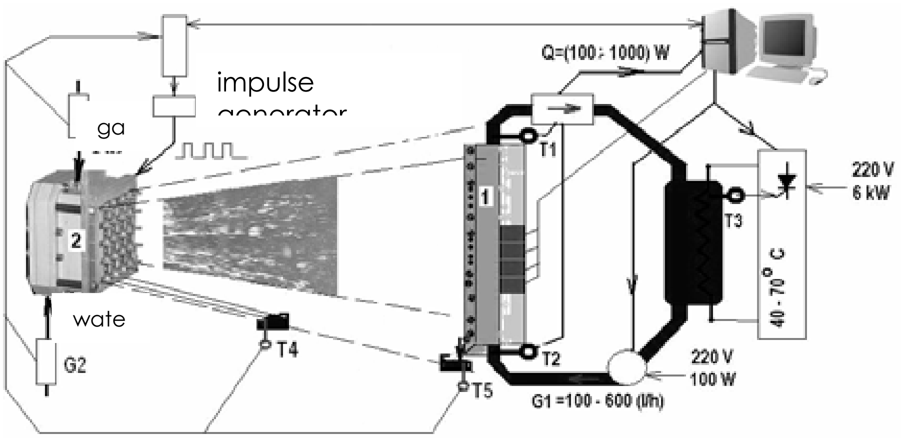


Fig. 1. Experimental stand supplied with a two-chamber mixer (for gas and water) as well as 16 horizontal nozzles (4 × 4) operated independently by means developed soft program.

way towards the heating surface was studied. The typical distribution of water-gas concentration profile in two dimensions is shown on the Fig 2.

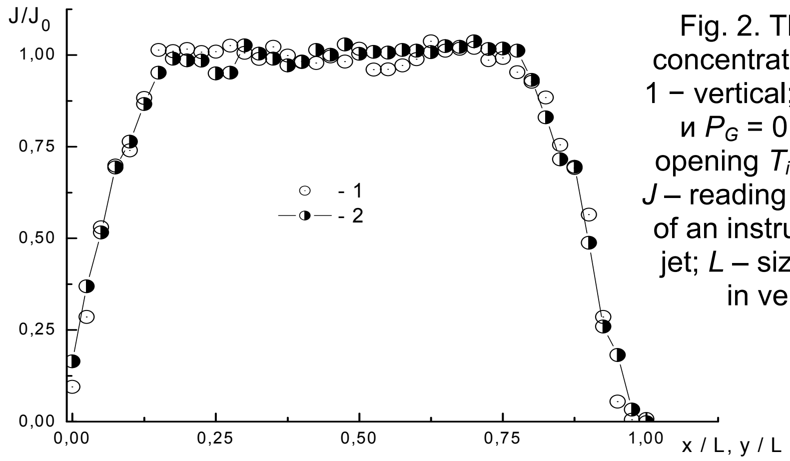


Fig. 2. The distribution of water-gas concentration profile in two dimensions: 1 − vertical; 2 – horizontal. P_W = 0.2 MPa и P_G = 0.1 MPa, time of liquid valve opening T_i = 3 ms, frequency F_i = 1 Hz. J – reading of an instrument; J_0 – reading of an instrument onto axis of two-phase jet; L – size of heat-exchanger surface in vertical and horizontal, m.

Note the deviation of liquid phase concentration profile measured on the distance L = 50 mm from the heat-exchanger’s surface was shown to be about 5%. The developed computer-controlled operation system was applied for experimental study of evaporative cooling the heating surface. It was shown that this system permits to tune effective heat exchange and provides effective cooling that is especially important for reactors performance in high exothermic chemical processes.

References

[1]. T. Li, K. Pougatch, M. Salcudean, D. Grecov. Numerical Simulation of an Evaporative Spray in a Gas-Solid Crossflow, International Journal of Chemical Reactor Engineering, **2010**, v. 8, p. 43.

[2]. Nazarov A.D., Serov A.F, Terekhov V.I, Sharov K.A. Experimental study of evaporative cooling with impulse spray. // Inzhenerno-Fizicheskii Zhurnal, **2009**, V.82, №6, p. 147.

[3]. Nazarov A.D., Terekhov V.I, Serov A.F. and K.A. Sharov K.A. An Experimental study of pulsed-spray impingement evaporative cooling // 7th International Symposium on Heat Transfer, (ISHT 08), October 26-29, **2008**, Beijing, China.

Acknowledgements

The research work was supported by RFBR Grant № 08-03-91758-AF (Russia).

DESIGN OF MONOLITHIC REACTORS FOR CONTINUOUS LIQUID-PHASE HYDROGENATION PROCESSES

Haase S., Bauer T., Lange R.

Technische Universität Dresden, Department of Chemical Engineering,
01062 Dresden, Germany;
e-mail presenting author: stefan.haase@tu-dresden.de

Recent research has shown that monolithic reactors are promising to intensify multiphase (gas-liquid-solid) reaction processes such as hydrogenations [1]. The performance enhancement results from several benefits of the uniform mini-structure, such as low pressure drop, low axial dispersion, high surface-to-volume ratio and easy reactor scale-up [2]. Based on numerical simulations, several investigators recommend the replacement of conventional catalyst particles by monolithic catalysts for fast reaction processes, such as hydrogenations, to increase space-time yield and selectivity [3, 4]. These theoretical findings are supported by experimental studies for the hydrogenation of diverse organic compounds in the liquid-phase [5]. The reactor performance strongly depends on the gas bubble length and the liquid slug length. In reaction studies reported, these parameters are roughly estimated or even unknown. Therefore, the optimal hydrodynamic conditions and consequently the maximum reactor performance are unknown, too. Furthermore, most of research work focused on superficial phase velocities above 100 mm/s in order to achieve a more uniform phase distribution at the reactor inlet and to the avoid hydrodynamic instabilities which can be caused by unfavourable gas-liquid mixing.

This work will present a novel setup to study hydrodynamic parameters (gas and liquid slug lengths) and overall reaction rates at elevated pressures and temperatures simultaneously for monolithic reactors. The gas bubble was formed inside the channel by feeding the gas with needle injectors. The gas bubble and liquid slug length at a given two-phase velocity was varied by the application of injectors with different outer diameters ranging from 0.4 mm to 0.8 mm and measured at the reactor inlet and at the reactor outlet.

In hydrodynamic studies, the range of superficial gas and liquid velocities to achieve slug flow for two-phase flow of alpha-methylstyrene and hydrogen has been examined (see Figure 1). The results reveal that stable and uniform slug flow exists even at superficial phase velocities of 10 mm/s and below.

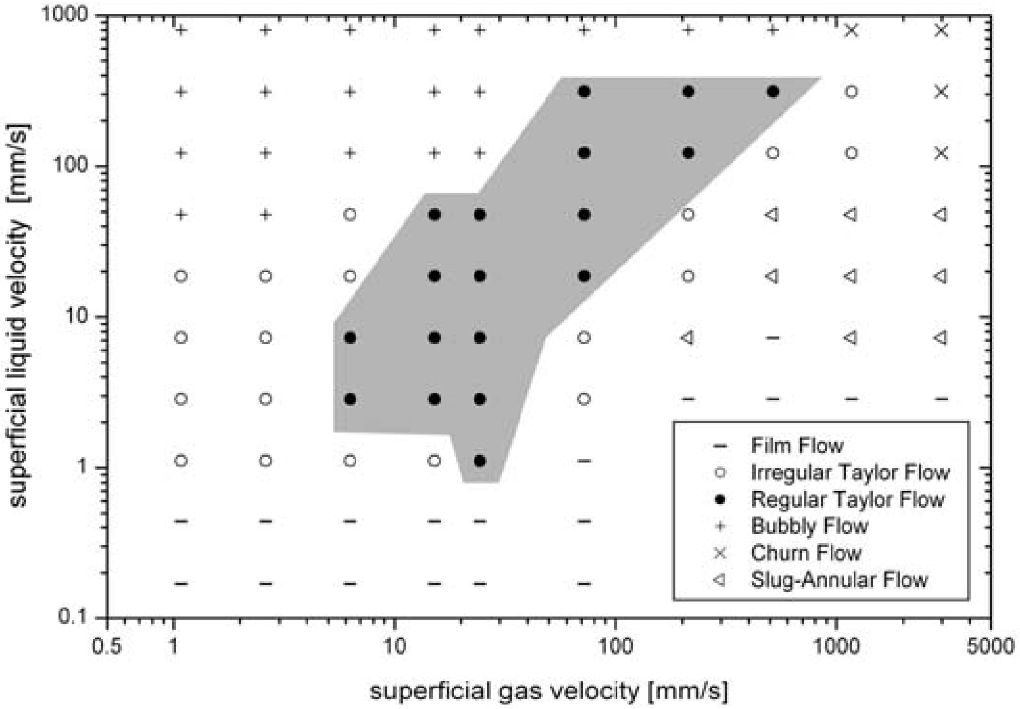


Fig. 1. Flow pattern map for alpha-methylstyrene/hydrogen two-phase flow in a square channel with a hydraulic diameter of 1.0 mm at a temperature of 298 K and a pressure of 1.0 MPa.

In reaction studies, the palladium catalyzed hydrogenation of alpha-methylstyrene to cumene at a pressure of 1.0 MPa has been performed in a coated monolithic channel. The influence of superficial liquid and gas velocities on reactor performance characterized by conversion per pass, space time yield and catalyst utilization are discussed and compared with the performance parameters of a conventional trickle-bed reactor.

References:

[1]. Dudukovic, M.P., Larachi, F; Mills, P.L. (**2002**). Catal. Rev. Sci. Eng., 44 (1), 123-246.

[2]. Boger, T., Zieverink, M.P., Kreutzer, M.T., Kapteijn, F., Moulijn, J.A. and Addiego, W.P. (**2004**). *Ind. Eng. Chem. Res.*, 43, 2337-2344.

[3]. Edvinsson, R. and Cybulski, A. (**1994**). Chem. Eng. Sci., 49 (248), 5653-5566.

[4]. Nijhuis, TA; Dautzenberg, FM; Moulijn, JA, (**2003**). Chem. Eng. Sci., 58 (7),1113-1124.

[5]. Enache, D.I., Landon, P; Lok, C.M. (**2005**). *Ind. Eng. Chem. Res.*, 44 (25), 9431-9439.

Acknowledgement:

The authors gratefully acknowledge the Deutsche Forschungsgemeinschaft (DFG) for financial support of the project.

OP-II-21

INTENSIFICATION OF CHEMICAL PROCESSES BY USING OF VORTEX BUBBLING LAYERS

Kuzmin A.O.[1,2], **Pravdina M.Kh.**[3], **Yavorsky A.I.**[4],
Yavorsky N.I.[2,3], **Parmon V.N.**[1,2]

[1]*Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia*
[2]*Novosibirsk State University, Novosibirsk, Russia*
[3]*Institute of Thermophysics, Novosibirsk, Russia*
[4]*Novosibirsk State Technical University, Novosibirsk, Russia*

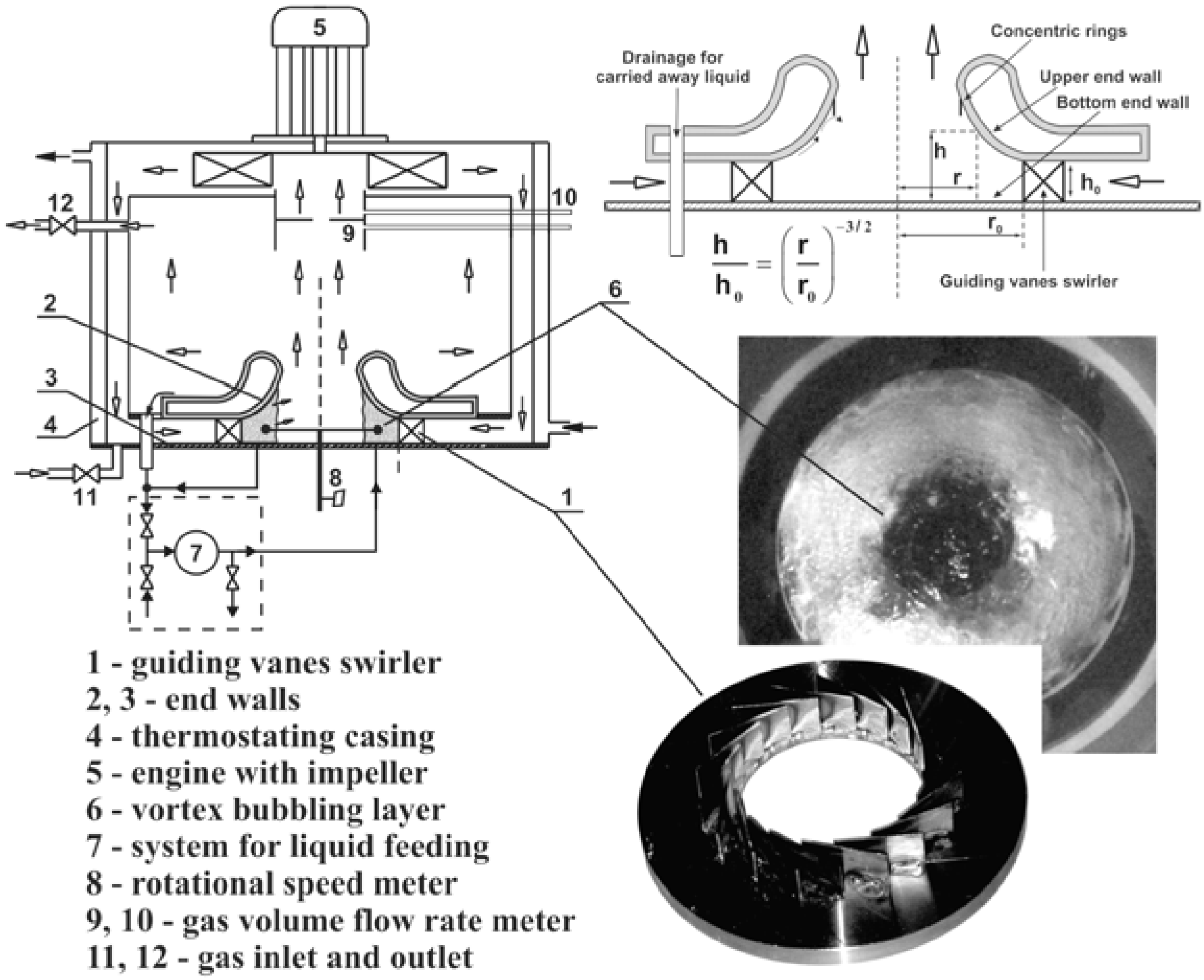
One of the topical tasks in modern chemical technology is efficient carrying out of chemical processes in the multiphase media. Currently, various types of multiphase gas-liquid reactors are used for accomplishing the multiphase reactions.

In the vortex multiphase device, a highly dispersed gas-liquid mixture is produced in the field of centrifugal forces inside the vortex chamber. The operation of the vortex chamber is based on the rotation of liquid by the tangential entry of gas flows via many tangential guiding vanes around the periphery of the vortex chamber. At certain regimes there appears a highly dispersed gas-liquid vortex bubbling layer.

The basic properties of vortex gas-liquid multiphase layers, principles of its stabilization, design of model vortex gas-liquid apparatuses are discussed.

The study of mass transfer efficiency in model vortex bubbling reactor has been carried out. The variation of Dankwerts's methods has been developed and used for determination of mass transfer parameters («k_L» – liquid side mass transfer coefficient, m/sec and «a» – effective gas-liquid interfacial area within vortex layer, m^{-1}). The method is based on consumption of CO_2 by carbonate buffer solution. It has been shown that maximum value of volumetric mass transfer coefficient «k_La» corresponds to the maximum stability of vortex bubbling layer and consists within the range of 7÷11 s^{-1} at used experimental conditions. It is established what the value of «k_La» only slightly depends on centrifugal acceleration of vortex layer. Comparison with other typical gas-liquid reactors has been made.

Homogeneous oxidation of alkaline sulfide solutions by air oxygen with only soluble products formation are demonstrated as effective chemical applications of vortex gas-liquid layers.



1 - guiding vanes swirler
2, 3 - end walls
4 - thermostating casing
5 - engine with impeller
6 - vortex bubbling layer
7 - system for liquid feeding
8 - rotational speed meter
9, 10 - gas volume flow rate meter
11, 12 - gas inlet and outlet

References

[1]. M.P. Dudukovic, F. Larachi, P.L. Mills, Multiphase catalytic reactors: a perspective on current knowledge and future trends, Catalysis Reviews - Science and Engineering, 44 № 1 (2002) 123 - 246

[2]. A.O. Kuzmin, M.Kh. Pravdina, A.I. Yavorsky, N.I. Yavorsky, V.N. Parmon, Vortex centrifugal bubbling reactor, Chemical Engineering Journal, 107 issues 1-3 (2005) 55-62

[3]. A.O. Kuzmin, V.N. Parmon, M.Kh. Pravdina, A.I. Yavorsky, N.I. Yavorsky, Patent RU № 2258559, № 2259870

[4]. M.A. Goldshtik, F. Hussain, R.J. Yao, The vortex liquid piston engine and some other vortex technologies, Sadhana 22 part 3 (1992) 323 – 367.

Acknowledgements:

The authors are very thankful for the financial support of the work by grants of RFBR (05-08-49995-a), SB of Russian Academy of Sciences "Integration program № 5".

MATHEMATICAL MODELLING OF THE PROPANE DEHYDROGENATION IN THE CATALYTIC MEMBRANE REACTOR

Shelepova E.V.[a], **Vedyagin A.A.**[a,b], **Noskov A.S.**[a,b]

[a]Boreskov Institute of Catalysis SB RAS, Pr. Ak. Lavrentieva, 5,
Novosibirsk, 630090, Russia, E-mail: shev@catalysis.ru
[b]Novosibirsk State Technical University, Pr. K. Marx 20,
Novosibirsk, 630092, Russia

The catalytic dehydrogenation of propane is a very demanding process which unfortunately has strong endothermic and equilibrium limitations. The oxidative dehydrogenation is an alternative way to produce propylene, but this process is characterized by low propylene selectivity. Using a membrane reactor permits one to increase the conversion value by the selective removal of hydrogen from the reaction zone and to shift the equilibrium towards the products.

The membrane reactor consists of two concentric tubes, where the interior ceramic tube with catalyst bed is placed in the exterior one. The exterior tube is the reactor shell. The membrane is deposited as a continuous layer on the outer surface of ceramic tube. The propane dehydrogenation reaction occurs over the catalyst in the tube side. Hydrogen permeates from the tube compartment of the reactor through the membrane to the shell compartment, where the hydrogen undergoes the oxidation. Selective hydrogen removal can significantly increase the propylene yield.

A mathematical model was developed to evaluate the performance of the dehydrogenation of propane in the catalytic membrane reactor. The two-dimensional non-isothermal stationary reactor model takes into account the mass and energy balance equations with the appropriate boundary conditions for tube and shell sides and for the ceramic support.

To describe the heat and mass transfer processes in the tube side the convective heat and mass transfer in the axial directions, diffusion and thermal conductivity in the radial directions, chemical reactions and heat effect of the reactions were taken into account. The diffusion and thermal conductivity in the radial directions were considered for ceramic support layer. Hydrogen flux has been proportional to the difference of the square roots of the hydrogen partial pressures across the membrane. In the shell side the heat and mass transfer processes were modeled by means of a one-dimensional plug-flow model: convective heat and mass transfer in the axial direction, flux of the hydrogen across the membrane, the catalytic reaction of the hydrogen oxidation and heat of hydrogen oxidation, heat transfer through the membrane and heat transfer at the reactor wall were taken into consideration.

The balance equations represent a system of differential equations in partial derivatives, which were treated numerically by the method of lines and the appropriate method for ODE solving.

Mathematical modelling permits us to investigate the influence of several relevant parameters of the model, such as inlet and wall temperatures, pressure and flow rate in the tube and shell sides, etc. on the process performance. The set of parameters for higher propane conversion and propylene selectivity were obtained.

The influence of hydrogen removal on the propane conversion and propylene selectivity in comparison with impermeable tube was shown. These values are essentially higher in the case of catalytic membrane reactor.

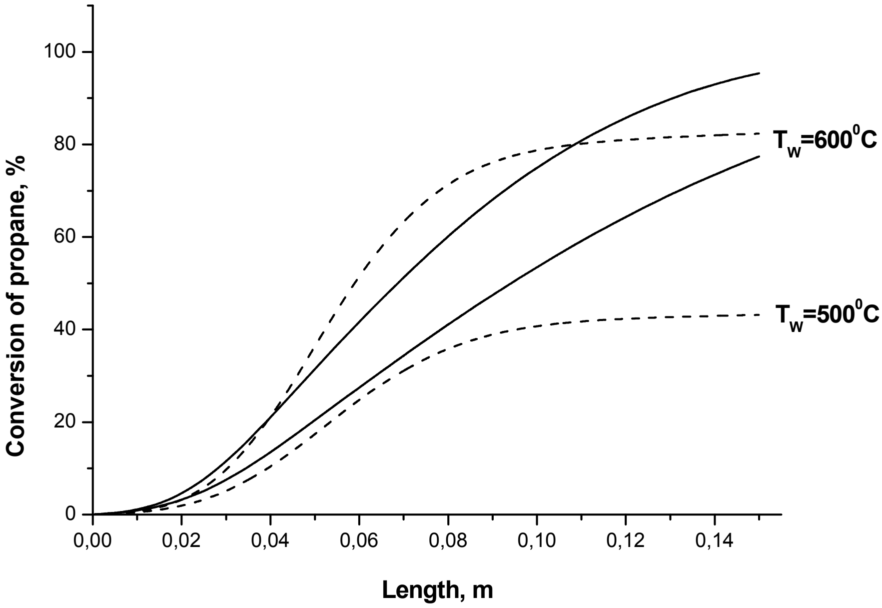


Fig. 1. Axial profiles of propane conversion for permeable (straight lines) and impermeable (dashed lines) tubes for different wall temperatures
$T_{Tube,in} = T_{Shell,in} = 200\,^{\circ}C$, $T_{Wall} = 500, 600\,^{\circ}C$,
$P_{tube} = 1.5$ atm, $P_{shell} = 1$ atm, G = 8.8 ml/min.

References

[1]. Abashar M.E.E., Al-Rabiah A.A. // Production of ethylene and cyclohexane in a catalytic membrane reactor // Chem. Eng. Proc. 44 (2005) 1188-1196.

[2]. M.P. Lobera, C. Tellez, J. Herguido, M. Menendes // Transient kinetic modelling of propane dehydrogenation over a Pt-Sn-K/Al_2O_3 catalyst // Applied Catalysis A: General 349 (2008) 156-164.

MICROWAVE-ASSISTED METHANOL STEAM REFORMING FOR HYDROGEN PRODUCTION

Durka T.[1], Stefanidis G.D.[1], Van Gerven T.[2] and Stankiewicz A.I.[1]

[1]Delft University of Technology, Process & Energy Department, The Netherlands,
g.stefanidis@tudelft.nl
[2]Katholieke Univ. Leuven, Department of Chemical Engineering, Belgium

The ability of microwaves to provide rapid heat directly into a catalytic bed has rendered microwave heating as a potential alternative to conventional heating requiring a heat transfer surface.[1] Moreover, microwave energy provides benefits unachievable in classical routes of heating. It has been reported that due to the interaction of microwaves with the catalytic bed, the catalytically-active phase can reach much higher temperatures than the surrounding support, the so called local hot spots.[2] This phenomenon is considered by some researchers to be responsible for the higher reaction rate and the improved selectivity observed under microwave heating.[3]

We have performed experimental work to investigate potential benefits stemming from the application of microwave energy to the methanol steam reforming reaction for hydrogen production. The study is focused on comparison of methanol conversion, product distribution and hydrogen selectivity over a range of operating conditions under two heating modes: electric vs. microwave. Special focus is given to the correct three-dimensional temperature mapping and hot spot detection in the catalytic bed.

The reaction is performed in a fixed-bed continuous-flow tubular glass reactor containing ca. 4 g of $CuZnO/Al_2O_3$ catalyst (Fig. 1). The catalyst pellets (3.2 mm) are placed at the bottom of the reactor and are supported by a glass fritz disk. The reactor is designed in such a way so that the reaction mixture of methanol, steam and nitrogen enters the reactor from the top in a bended glass tube (thick red line in Fig. 1), which crosses the catalytic bed right at the center; the reactants exit the tube below the catalytic bed and then flow upwards through the catalytic bed after they have been radially distributed by the porous glass disk. Finally, the exhaust gas is released from the top-right part of the reactor (Fig.1).

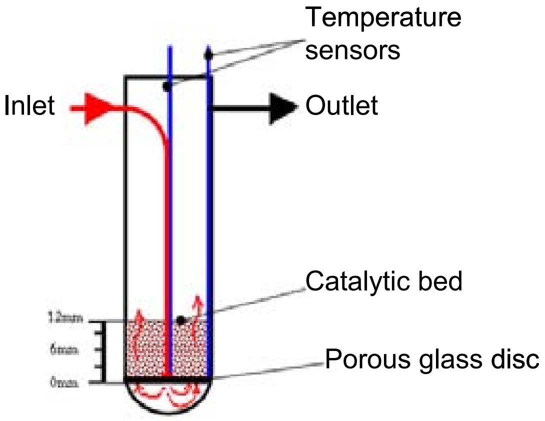


Fig. 1: Schematic view of the steam reforming reactor with two immersed fiber optic probes

The effluent gas is dried in a cold trap at ca. -15°C and then analyzed with on-line gas chromatography. The unreacted liquid phase is collected in the cold trap and analyzed at the end of the experiment in order to determine the methanol conversion. The temperature in the catalytic bed is measured by two fiber optic (FO) sensors placed in the center and close to the reactor wall (thick blue lines). The probes are introduced in the reactor through a 2 mm O.D. capillaries in order to allow for change in the axial (vertical) position and thus temperature measurement in various heights. The obtained temperature measurements are used to determine an average temperature in the catalytic bed during the reforming reaction under steady-steady conditions.

It has been observed that methanol conversion under microwave heating is significantly higher than that achieved with conventional electric heating under approximately similar bulk temperature conditions (Fig. 2). The observed effect can be rationalized by the presence of hot spots formed at the metal catalyst particles, which are better microwave absorbers than the support itself. This important finding, which qualitatively holds over a range of operating conditions (different flow rates, steam-to-carbon ratios and temperature levels), implies significant benefits in terms of higher energy efficiency and improved process safety.

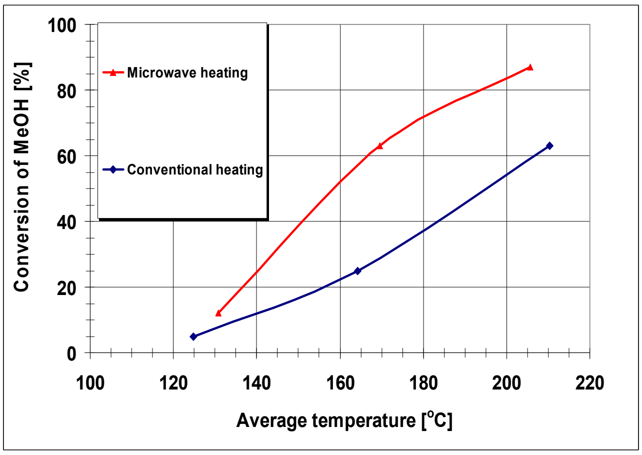


Fig. 2: Methanol conversion vs. average reactor temperature under microwave and conventional heating.

References

[1]. Perry W. L., Datye A. K., Prinja A. K., Brown L. F., Katz J. D. Microwave heating of endothermic catalytic reactions: Reforming of methanol. *AIChE Journal* **2002,** 48, (4), 820-831.

[2]. Ioffe M. S., Pollington S. D., Wan J. K.S., High-Power Pulsed Radio-frequency and Microwave Catalytic Processes: Selective Production of Acetylene from the Reaction of Methane over Carbon. *Journal of Catalysis* **1995,** 151, (2), 349-355.

[3]. Chemat-Djenni Z., Hamada B., Chemat F., Atmospheric Pressure Microwave Assisted Heterogeneous Catalytic Reactions. *Molecules* **2007,** 12, (7), 1399-1409.

OP-II-24

MODELING OF A CATALYTIC PLATE REACTOR PRODUCING HYDROGEN FOR FUEL PROCESSOR SYSTEMS

Kırçın R.M., Karakaya M., Avcı A.K., Aksoylu A.E., Önsan Z.I.

Department of Chemical Engineering, Bogazici University, Bebek 34342,
Istanbul, Turkey, onsan@boun.edu.tr

The need for careful temperature control and energy integration as well as the cost of valuable metal catalysts and elimination of pore diffusion effects has compelled research in the direction of process intensification through design of structured reactors and use of alternative catalysts [1]. The catalytic plate reactor (CPR) constitutes a good example for structured reactors by which conventional packed-bed reactors can be sized down due to intensification of heat and mass transfer [2]. The CPR itself is a cascade of closely spaced plates coated with catalyst on both faces. If catalyst coatings on the two faces of the plate are different, significant heat transfer intensification can be achieved by running an endothermic reaction on one face and an exothermic reaction on the other face of the plate for supplying the energy required by the endothermic reaction [3-4].

The aim of this work was mathematical modeling and steady-state as well as dynamic simulation of a catalytic plate reactor (CPR) in which hydrogen is produced by a reaction pair, namely, endothermic ethanol steam reforming coupled with exothermic methane total oxidation. The two-dimensional heterogeneous model used included conservation of momentum, mass and energy to describe reactor performance in steady-state operation as a function of operational and dimensional parameters such as feed composition on different sides of the plate including water-to-hydrocarbon and oxygen-to-hydrocarbon ratios, plate material and wall thickness. Further, the start-up behavior of the reactor was also analyzed by dynamic simulations to follow spatial and temporal evolutions of transients. The kinetic expressions related to rates of methane catalytic total oxidation and ethanol steam reforming were taken from the literature [5-6]. The coupled, two-dimensional steady state and transient model equations were solved using the finite element method through the COMSOL Multiphysics™ CFD package.

Simulations using stoichiometric feed ratios of reactants and standard materials of construction resulted in small transverse and axial temperature gradients, smooth temperature profiles, no hot spot formation and realistic reactor performance in terms of reactant conversions. Parametric studies conducted by variation of plate material and wall thickness led to minor changes in thermal patterns and indicated no significant effects on reactor performance. In contrast, variations in operational parameters such as water-to-hydrocarbon and oxygen-to-hydrocarbon ratios resulted in notable changes in reactor output. In ethanol steam reforming, water-deficient feed in the reforming channel reduced ethanol conversion and hydrogen production dramatically. Any reduction in the oxygen content of the total oxidation channel caused methane conversion values to be significantly lower, leading to lower heat production and consumption rates. Dynamic simulations conducted for analyzing reactor start-up behavior showed that the temporal and spatial evolutions of transients converge to the steady state solution.

References

[1]. Qi, A., Peppley, B. and Karan, K., Fuel Processing Technology, **2007**, 88, 3-22.

[2]. Zanfir, M. and Gavriilidis, A., Chem. Eng. Sci., **2001**, 56(7), 2671-2683.

[3]. Zanfir, M. and Gavriilidis, A., Chem. Eng. Sci., **2003**, 58, 3947-3960.

[4]. Ramaswamy, R. C., Ramachandran, P. A. and Dudukovic, M. P., Chem. Eng. Sci., **2006**, 61, 459-472.

[5]. Ma, L. and Trimm, D. L., Appl. Catal. A: Gen., **1996**, 138(2), 265-273.

[6]. Karakaya, M. and Avci, A. K., Top. Catal. **2009**, 52, 2112-2116.

Acknowledgements

Financial support provided by Bogazici University projects BAP-06A503, BAP-08A503, DPT-07K120630 and TUBITAK project 104M163 is acknowledged.

MULTISCALE ANALYSIS OF A COATED-WALL MICROCHANNEL REACTOR

Lopes J.P.[1], **Cardoso S.**[2], **Rodrigues A.**[1]

[1]*Associate Laboratory LSRE/LCM, Faculty of Engineering, University of Porto, Porto, Portugal, deq07006@fe.up.pt*
[2]*Department of Chemical Engineering and Biotechnology, University of Cambridge, Cambridge, UK*

Microreactor technologies have been object of intense research due to the reduced mass/heat transfer resistance compared with conventional equipment[1]. Applications of these microsystems range from production of fine chemicals, pharmaceuticals and energy-related compounds (e.g. synthesis gas and hydrogen for fuel cells) to biotechnological products (from e.g. immobilized enzymes in a coated-wall biomicroreactor), catalyst screening and analytical measuring devices[2].

The interest in using such devices relies on the maximization of fluxes by increasing transfer areas. Also, the characteristic times for transverse diffusion and conduction are faster. The surface reaction effects are then favoured, and a catalytic porous coating is frequently attached to the wall of the microchannel, providing a larger total solid surface area, where heterogeneous reactions can take place. Although thin layers are typically found, it is possible in general to consider internal mass transfer limitations[3]. Then, the physical picture involves transport of reactants in a fully developed channel flow by convection and axial diffusion and by radial diffusion towards the washcoat. Inside the catalyst layer, further diffusion through the porous media occurs, together with reaction at the active sites.When diffusional limitations inside the washcoat are not negligible, the interaction between transport in the channel and reaction-diffusion processes in the porous layer determines the performance of the microchannel reactor. The same problem is relevant in the context of processes with catalytic monoliths[4] and hollow-fiber membrane reactors[5], e.g.. Efficient modelling techniques have already been developed for surface wall catalysed reactions with no internal mass transfer resistance[6].

In this contribution, a rigorous scaling analysis[7,8] of the general coupled problem of transport in a microchannel with reaction-diffusion processes occurring at the washcoat is presented. This results in order-of-magnitude criteria for common modeling assumptions, such as: negligible transverse gradients, reduction to the (surface) ‘wall-reaction’ model (negligible concentration gradients inside the catalytic layer) and reactant exhaustion at the washcoat wall due to fast reactions.

The system behaviour is described by dimensionless parameters translating the competition between the characteristic times for transport mechanisms and/or heterogeneous reaction and depend on flow properties, geometrical relations (e.g. aspect ratio, washcoat thickness) and reaction kinetics. This multi-scale analysis will contribute for the selection of suitable models for simulation in specific parameter ranges, since operating regimes are mapped and analytical solutions available for the relevant ones. Moreover, the ranges of validity of such regimes constitute the boundaries in the aforementioned parametric diagrams. For each regime, approximate concentration profiles are derived and simple estimates for the conversion (or equivalently, the mixing-cup concentration) provided. As a consequence, the classical Graetz problem will be reencountered in the commonly found regime where convection and transverse diffusion are dominant. In this case, the main results are reviewed and systematized in the common multiparametric analysis.

Finally, the analytical approach employed results in a shortcut method for design and preliminary optimization of microreaction units. On the other hand, simplification of the numerical procedure may be achieved by introduction of approximate analytical solutions in the regimes of interest.

References

[1] P. L. Mills, D. J. Quiram and J. F. Ryley, Chem. Eng. Sci. **2007**, *62*, 6992-7010.

[2] W. Ehrfeld, V. Hessel and V. Haverkamp in *Microreactors*, *Vol.* Wiley, **2005**.

[3] S. Walter, S. Malmberg, B. Schmidt and M. A. Liauw, *Catal. Today* **2005**, *110*, 15-25.

[4] M. Bhattacharya, M. P. Harold and V. Balakotaiah, *Chem. Eng. Sci.* **2004**, *59*, 3737-3766.

[5] W. Lewis and S. Middleman, *AIChE J.* **1974**, *20*, 1012-1014.

[6] T. Gervais and K. F. Jensen, *Chem. Eng. Sci.* **2006**, *61*, 1102-1121.

[7] C. M. Bender and S. A. Orszag, *Advanced Mathematical Methods for Scientists and Engineers* **1978**.

[8] C. C. Lin and L. A. Segel, *Mathematics Applied to Deterministic Problems in the Natural Sciences*, SIAM, **1988**

Acknowledgements

J. P. Lopes gratefully acknowledges financial support from FCT - Fundação para a Ciência e a Tecnologia, PhD fellowship SFRH/BD/36833/2007.

DESIGN, SCALE-OUT AND OPERATION OF MILLI-CHANNEL REACTOR WITH STRUCTURED Ni/CeO_2 CATALYST FOR PREFERENTIAL CO METHANATION

Popova M.M.[1,2], **Snytnikov P.V.**[1,2], **Amosov Yu.I.**[1,2], **Kuzmin V.A.**[1],
Shigarov A.B.[1,2], **Kirillov V.A.**[1,2], **Sobyanin V.A.**[1,2]

[1]Boreskov Institute of Catalysis SB RAS, Pr. Lavrentieva, 5, Novosibirsk, 630090, Russia, popovamm@catalysis.ru
[2]Novosibirsk State University, Pirogova St., 2, Novosibirsk, 630090, Russia

Preferential CO methanation in the presence of CO_2 is one of the promising methods for CO removal from hydrogen-rich gas mixtures produced by hydrocarbons conversion processes for feeding of the low temperature polymer electolyte membrane fuel cells. Compared to preferential CO oxidation reaction, preferential CO methanation is a more feasible process as it uses no oxygen (air), hydrogen-rich gas is not diluted with nitrogen and allows reducing CO level to <100 ppm in a wider temperature interval. The generated methane is tolerated by PEM FC and can be utilized in an anode gas afterburner. Since the CO concentration in the hydrogen-rich gas is not high, the CO methanation reaction consumes small amount of hydrogen.

The main problem is competitive CO_2 methanation. The concentration of CO_2 considerably exceeds that of CO in hydrogen-rich gas mixtures produced by hydrocarbons reforming processes. CO_2 can also undergo methanation that leads to considerable hydrogen losses. Besides, reverse water gas shift reaction can facilitate CO formation. Therefore, there is a need for highly selective catalysts that allow CO cleanup, but not CO_2 methanation.

The aim of the present work was to optimize structure and composition of the active and highly selective nickel-cerium oxide catalyst proposed ealier [1, 2] for the reaction of preferential CO methanation in hydrogen-rich gas mixtures in the presence of CO_2 and to design a reactor for deep purification of syngas from CO.

The catalysts performance for selective CO methanation in H_2 excess was studied in a flow setup with on-line chromatographic analysis of the reaction products. The dependencies of the catalyst performance on the temperature, inlet composition and feed rate of the gas mixture have been determined. The experiments were performed at GHSV = $5000 \div 80000\ h^{-1}$ and temperatures $160 \div 400$°C.

It was found that the 10 wt.% Ni/CeO_2 catalyst showed good performance and decreased the CO concentration to <100 ppm in a wide temperature interval with high selectivity (Figure 1).

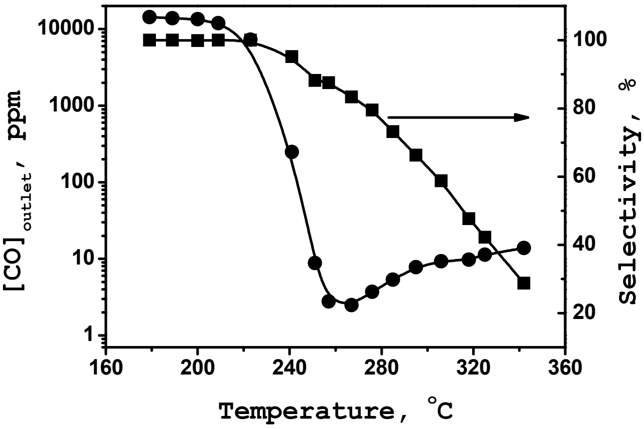


Figure 1: The temperature dependencies of CO concentration and selectivity of CO methanation on 10 wt.% Ni/CeO_2. The inlet gas mixture composition (vol.%): CO –1.5, CO_2 – 20, H_2O – 10, H_2– balance. GHSV = 40000 h^{-1}.

Figure 2: Milli-channel reactor with structured 10 wt.% Ni/CeO_2 catalyst for preferential CO methanation.

Since selective CO methanation is highly exothermic reaction, efficient heat management is needed to maintain high selectivity. For this purpose, 10 wt.% Ni/CeO_2 catalyst was supported onto plane and corrugated metal gauzes. Being arranged one by one in alternate order, the plane and corrugated strips formed a system of reaction channels. On this base, a milli-channel reactor with structured catalyst was developed (Figure 2). Testing of the reactor integrated into fuel processor showed that it allowed the decrease of CO concentration to <100 ppm as the outlet temperature was kept below 300 °C. In the tests, the syngas flow rate was 8 m^3/h, the reactor volume – 3 L, catalyst weight – 0.32 kg, the inlet synthesis gas composition (vol.%): H_2O – 17,7; CO_2 – 15,8; CO – 0,78; H_2 – 65,5; CH_4 – 0,2.

The results obtained proved the nickel-ceria catalysts and the structured reactor to be quite promising for efficient CO removal from hydrogen-rich gas mixtures and therefore attractive for low-temperature PEMFC applications.

References

[1]. Badmaev S.D., Snytnikov P.V., Int. J. Hydrogen Energy, **2008**, Vol. 33, P. 3026.
[2]. Snytnikov P.V., Semin G.L., Sidyakin M.V. Sobyanin V.A., RU Patent 2 323 044.

Acknowledgements

The work was partially supported by grant “UMNIK“ of the FASIE, MK-5602.2010.3 (grants of Russian Federation President) and GC №P1015 of FFP “SSESIR 2009-2013”.

REACTOR WITH SELECTIVE MICROWAVE HEATING OF CHEMICAL REAGENTS AND ITS APPLICATION FOR CATALYTIC PYROLYSIS OF HEAVY HYDROCARBONS

Udalov E.[1], Tanashev Yu.[1], Bolotov V.[1], Bobrova L.[1], Parmon V.[1,4],
Chernousov Yu.[2], Chumakov Yu.[3], Knyazeva A.[3]

[1]*Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia, udalov@catalysis.ru*
[2]*Institute of Chemical Kinetics and Combustion SB RAS, Novosibirsk, Russia*
[3]*Institute of Strength Physics and Materials Science SB RAS, Tomsk, Russia*
[4]*Novosibirsk State University, Novosibirsk, Russia*

It is well known that absorption of microwaves by any substance is sensitive to the nature of irradiated material, so the microwave (MW) power can be used for selective heating of heterogeneous systems. The approach of non-uniform heating of a system containing different chemical reagents is used in the present work for performing and modeling the decomposition of liquid hydrocarbons, which are not absorbing MW, in the presence of solid catalyst possessing high MW absorbency. The endothermic process is performed under high temperature, over 650K, so, first, a considerable amount of heat is supplying to the catalyst and, second, the thermal decomposition occurs in a non isothermal three-phase system “solid catalyst + liquid reagent + gaseous products”.

For the experiments on MW heating of mixtures “catalyst + liquid hydrocarbons”, we designed special MW cavities of high quality (with large “Q factor”). The possibility of (i) resonance frequency tuning, (ii) changing the coupling coefficient, (iii) placing the investigated sample into the maximum of both magnetic (Cavity 1) and electric (Cavity 2) field and (iv) measuring the efficiency of MW absorption have been envisaged. The MW power density absorbed by the catalyst can reach at least 100W per 1g. As the pyrolysed reagents, *n*-hexadecane $C_{16}H_{34}$ (the boiling temperature 560K), fuel oil (viscous mixture of hydrocarbons C_{16+}) and viscous Mongolian oil with the high content of heavy paraffin have been used without preliminary heating. As the catalysts, some materials with good microwaves absorbency have been chosen: granules of a cermet Al_2O_3/Al (hydrothermally synthesized from powdered aluminium), “magnetocenospheres” (a fraction of flying ash of coal combustion with high content, 90%wt., of iron oxide), granulated zeolite, artificial porous graphite-like material Sibunit, fiberglass which can be used as a catalyst support and fiberglass with deposited Pd. The catalysts were loaded to a quartz reactor of both flow and non-flow type. During the MW heating of the catalyst, the vaporized reaction products were directed to a condenser. The liquid as well as the gaseous (non-condensed) products have been analyzed by GLC method.

During the experiments, we observe intense heating of the catalysts used, and it leads to boiling of hydrocarbons and formation of vaporized products. The products composition for all reagents used, as a rule, includes hydrogen, liquid and gaseous (C_2H_4, C_3H_6 and CH_4 mainly) hydrocarbons which are lighter than the initial ones. The specific feature of the MW-assisted hexadecane pyrolysis is the predominant formation of α-olefins as the main products. Selectivity of the α-olefins formation exceeds 80% for the next catalysts: cermet, magnetocenospheres and Pd/Fiberglass. In the presence of zeolite or fiberglass, the formation of alkanes is more expressed. Note that all materials demonstrating high selectivity in respect to the olefins formation are composites which include small metal particles. One can suppose that under microwaves these catalysts are heated non-uniformly. The presence of small overheated particles promotes the α-olefins formation because of the olefins concentration must increase with the temperature rising. On the other hand, this selectivity is additionally reinforced by the “quenching” effect. Indeed, alpha olefins are known to be the primary products of thermal decomposition of long alkane molecules. Under conditions of ordinary heating, these primary products may decompose as a result of secondary reactions. On the contrary, under MW heating, the primary products of the thermal decomposition appear to be immediately in contact with the much colder liquid reagent, which provides their rapid cooling (quenching).

Using a mathematical simulation, the model of the decomposition initiation in the vicinity of an individual MW-absorbing catalyst particle has been formulated and studied. It is shown that there are some critical conditions of the reaction initiation depending on the particles properties and parameters of the MW radiation. The model of the hydrocarbon decomposition in the vicinity of an individual MW-absorbing catalyst particle allowing the effects of thermal expansion is considered.

Acknowledgements

Financial support from Russian Academy of Sciences under Project No.2 of the Basic Research Program 19 is gratefully acknowledged. The work is also supported by Siberian Branch of Russian Academy of Sciences under Integration Ordered Project No.5.

ORAL PRESENTATIONS

SECTION III

Chemical Reactors and Technologies for Emerging Applications

Section III-A

Processing of Biomass and Renewable Feedstocks

A NEW SIMPLE MICROCHANNEL DEVICE FOR INTENSIFYING BIODIESEL PRODUCTION

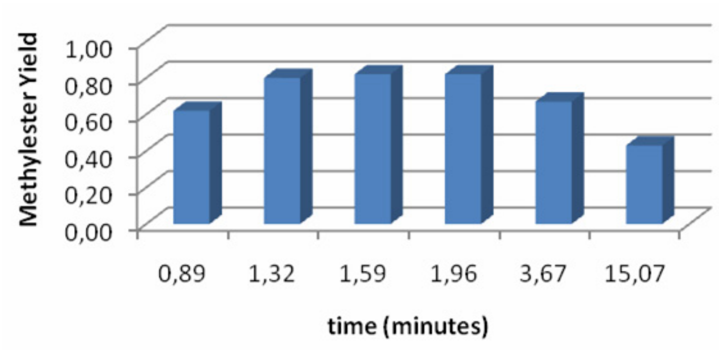
<u>Santacesaria E.</u>[1], Di Serio M., Tesser R., Russo V., Turco R., Tortorelli M.

University of Naples "Federico II" – Department of Chemistry,
Complesso Universitario Monte S. Angelo, Via Cintia 4, I-80126 Naples (Italy)
[1]E-mail address: elio.santacesaria@unina.it - Fax: +39 081674026

In the present work a new laboratory device, recently patented[1], specifically developed to obtain microchannels, in order to test the process intensification effect on different reactions will be described. This device represents a useful connection between a traditional tubular packed bed reactor and the microreactors that are very efficient, as it is well known, in mass and energy transfer operations. The apparatus developed in this work is constituted by a tubular reactor which packing is composed by metallic spheres with different diameters and/or of filling material of different shape and size. The filling material size is chosen in a way that the cavities between the particles promote a very active local micromixing. In the obtained packing of the tubular reactor, microchannels are present with variable sizes in a range between 200-2000 μm, values that are comparable with those of the commercially available microreactors. Moreover, with microchannels of these sizes, an intensive mixing is realized also at relatively low flow rates, enhancing the mass transfer effect, in particular in the case of immiscible liquid phases, while, the metal thermal conductivity allows a fast heat exchange.

The transesterification reaction of vegetable oil with methanol, promoted by potassium or sodium hydroxide or related alkoxides, is characterized by the immiscibility of the reagents. Therefore, the reaction is strongly enhanced by an efficient stirring and is, therefore, particularly suitable to be conducted in a microreactor in which micromixing is very active. Moreover, this aspect can be better profited by increasing the temperature above the boiling point of methanol (65°C), obviously operating at higher pressure. In this case the reaction rate increases more and more but, due to micromixing, the reaction is not limited by the mass transfer. This behavior has recently been demonstrate by using, for producing biodiesel, a Corrugated Plates Heat Exchanger (CP-HEX reactor) as reactor[2,3]. As this reaction is athermic the operation is safe and the isothermicity can easily be achieved. We will demonstrate in this work that by using a tubular reactor filled with spheres or filling materials with other shapes of opportune size we can increase the local micromixing and consequently the activity and yields.

First of all, in this work the fluid dynamic behavior of a tubular reactor, simply filled with stainless steel balls of uniform size, has been examined with a step test. This tubular reactor has a length of 20 cm, an internal diameter of 1 cm, an empty volume of 15.7 cm^3, a void volume after the filling of 6.8 cm^3 and contained about 2000 spheres of 2.5 mm of diameter. From this preliminary study we have concluded that the reactor is locally well mixed for relatively low flow rates above 5.6 cm^3/minute corresponding to a Reynolds Number of 2.17 and a Peclet of 30. Different transesterification kinetic runs have then been performed on soybean oil with methanol, in the presence of KOH catalyst, for different overall flow rates of the reagents that have been kept at constant molar ratio. Flow rates were changed from 0.73 to 12.3 cm^3/minute respectively corresponding to 15.07-0.89 minutes of residence time. It is interesting to observe that the achieved yields in biodiesel increased by decreasing the residence time till to reach a maximum value in correspondence to a residence time of 1.59 minutes (see the figure), then we observe a decrease, as expected when the chemical regime is completely attained.



The work proceeds by considering what happens when the cavities between the spherical balls of 2.5 mm of diameters are filled with smaller balls of 0.39 mm. In this case, microchannels of about 300 μm are formed and the described device operates like a microreactor, but the kinetic approach can be assimilated to that of a plug flow tubular reactor. At last, filling material of different shape and size more suitable than spheres to induce local micromixing will be tested on the same reaction. Another objective of this work is to ascertain the intrinsic kinetics of the transesterification reaction, because, the operative conditions can be chosen in such a way to eliminate mass transfer limitation.

References

[1]. E. Santacesaria, M. Di Serio, R. Tesser; Italian Patent Na2009A000024, 2009 Assigned to EUROCHEM Engineering.

[2]. E. Santacesaria, M. Di Serio, R. Tesser, L. Casale, D. Verde, R. Turco, A. Bertola; Energy Fuels 2009, 23, 5206–5212.

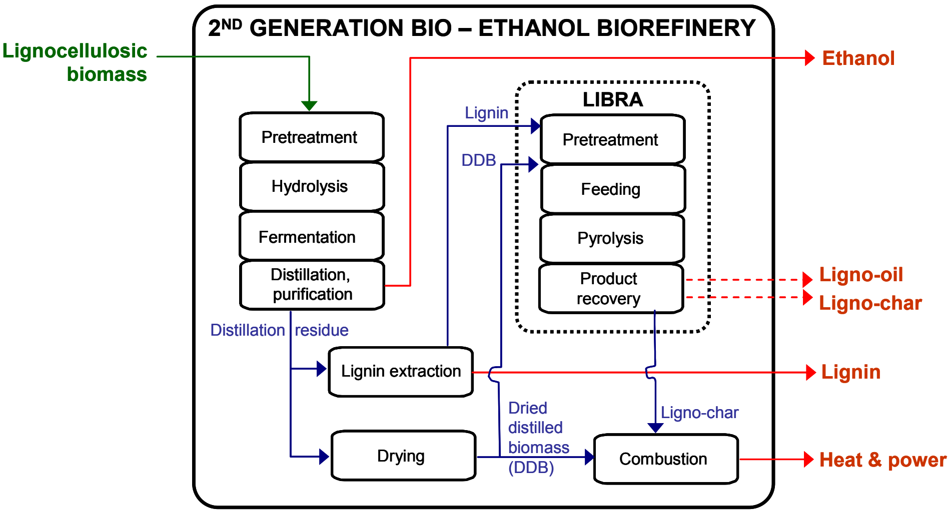
[3]. E. Santacesaria, M. Di Serio, R. Tesser, R.; R. Turco, D. Verde, L. Casale, Italian Patent I2008A002302, Dec. 2008 assigned to MYTHEN SpA Co.

BUBBLING FLUIDISED BED PYROLYSIS OF LIGNIN FOR VALUE-ADDED PRODUCTS

Paul de Wild, Ron van der Laan, Ruud Wilberink

Energy research Centre of the Netherlands (ECN),
Westerduinweg 3, 1755 LE Petten, The Netherlands
E-mail: dewild@ecn.nl

Lignin is a large waste stream from the pulp- and paper industry and 2nd generation biorefineries for biofuels.

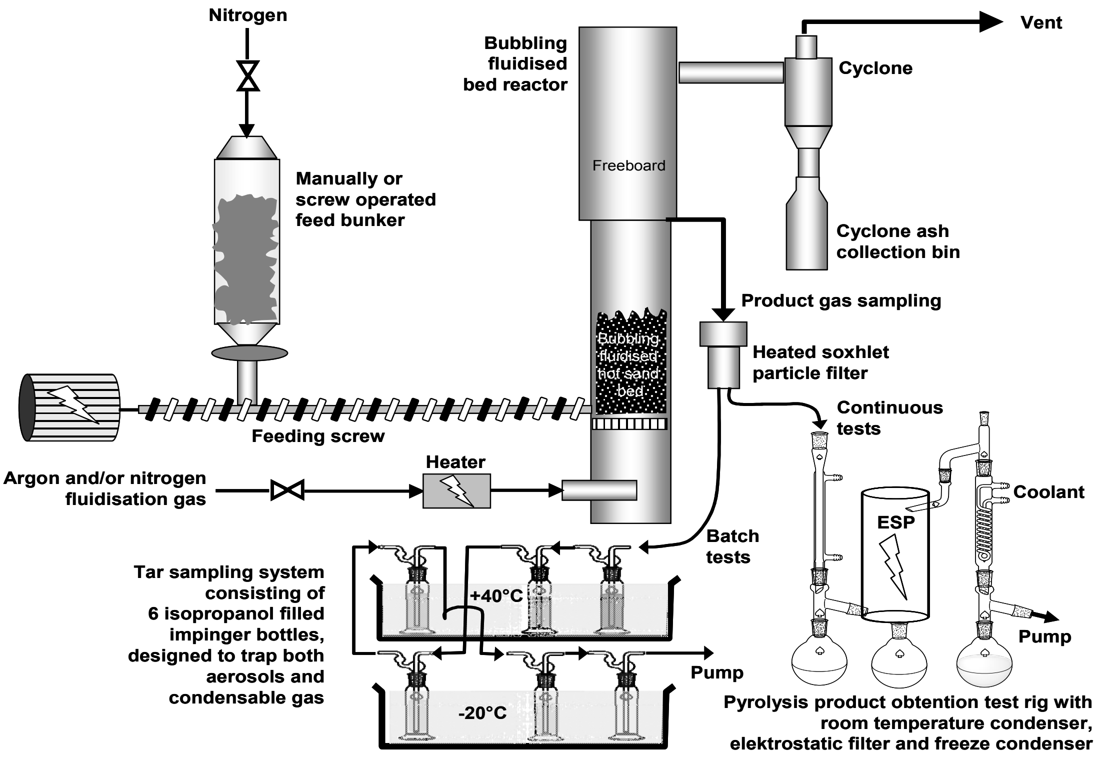


Although lignin is an interesting petrochemical substitution option for fuel, polymers and individual chemicals, industrial lignin pyrolysis processes are rare. In literature, yields of mono-phenolic compounds are reported that rarely exceed 5-6 % [1,2]. Consequently, the main practised option for lignin is the use as fuel for generating heat.

LIBRA is a new Lignin BioRefinery Approach based upon bubbling fluidised bed pyrolysis technology [3] to valorise lignin in a phenolic bio-oil and bio-char for applications such as phenol subtitutes in wood-resins, high-value phenolics as precursors for pharmaceutical, food, and/or transportation fuel applications, soil improver, growth enhancer and filtration material.

Three lignins derived from hardwoods, from a mixture of grass and straw, and from annual plants as a raw residue from the production of bio-ethanol have been processed according to LIBRA to investigate their potential as renewable feedstocks for valuable products.

Continuous pyrolysis experiments were conducted using a specially adapted atmospheric pressure, 1 kg/hr bubbling fluidised bed test facility at 400°C (see figure below) featuring automated operation and data acquisition. Feedstocks, solid, liquid and gaseous products were analysed using standard analysis methods like TGA, GC/MS, ND/IR, BET, NMR, SEM, etc.



Results indicate that lignin can be valorised in bio-char (40%) and bio-oil (40%). The bio-oil contains 16-21 wt% (d.b.) of a phenolic fraction constituting of monomeric (6-10%) and oligomeric (10-13%) compounds. LIBRA clearly indicates the potential for pyrolysis to valorise lignin.

The lignins were provided by Dr. R. Gosselink from Wageningen University Research, The Netherlands Prof. A.V. Bridgwater of Aston University, UK and a biorefinery developer.

REFERENCES

[1]. Antal, M.J., Jr., ‘Biomass pyrolysis: a review of the literature, Part 2 – lignocellulose pyrolysis’, In: Advances in Solar Energy, 1985, Vol. 2, Chapter 4, pp. 175 – 255.

[2]. Allan, G.G. and Matilla, T., ‘High energy degradation’, In: ‘Lignins: Occurrence, Formation, Structure and Reactions’, edited by K.V. Sarkanen and H. Ludwig, 1971, Chapter 14, pp. 575-592.

[3]. De Wild, P.J., Van der Laan, R., Kloekhorst, A., Heeres, E., 'Lignin Valorisation for Chemicals and (Transportation) Fuels via (Catalytic) Pyrolysis and Hydrodeoxygenation', Environmental Progress and Sustainable Energy, 28, 3, 2009, 461 – 469.

PINEWOOD PYROLYSIS UNDER VACUUM CONDITIONS IN A CONICAL SPOUTED BED REACTOR

Amutio M., **Lopez G., Artetxe M., Elordi G., Olazar M., Bilbao J.**

Chemical Engineering Department, University of the Basque Country, PO Box 644
E48080 Bilbao, Spain. Phone: +34 94 601 5414, e-mail: maider.amutio@ehu.es

Biomass is considered one of the most interesting alternatives to fossil fuels, since adequately used it does not contribute to a net rise in the level of CO_2 in the atmosphere. Flash pyrolysis of biomass is one of the most promising techniques that may enable this raw material to become a viable alternative to oil. The interest of vacuum pyrolysis lies in the advantages associatee with the decresae in the inter gas flowrate and residence time of volatiles in the reactor [1]. Conical spouted bed reactor is a suitable reactor for solids that are difficult to handle, irregular or sticky, as biomass [2], because of the good contact between the gas and the solid phase.

Pine (pinus insignis) sawdust pyrolysis has been carried out in a conical spouted bed reactor, provided with a system for continuous feeding of biomass (Figure 1). The bed was initially made up of 100 g of sand, allowing the continuous removal of the char from the bed by a lateral outlet. The experiments have been carried out at 500 °C and two pressure levels: 0.25 and 1 atm. Product stream components have been analyzed online using a Varian 3900 chromatograph, injecting the samples to the GC by means of a thermostated line maintained at 260 °C.

The products obtained in the pinewood pyrolysis have been grouped into four different fractions: gas, bio-oil, water and char. The results of the obtained yields are summarized in Table 2.

Table 2. Effect of pressure on pinewood pyrolysis product yields (% wt, wet basis).

Fraction	500 °C, 1 atm	500 °C, 0.25 atm
Gas	7.3	7.4
Bio-oil	50.0	52.3
Water	25.4	25.0
Char	17.3	15.3

As it is observed, high yields of liquid are obtained in both vacuum and atmospheric pyrolysis in the conical spouted bed reactor. However, product yields are hardly affected by reaction pressure and the major difference is that a 2 % more of bio-oil is obtained. Gas fraction is mainly composed of CO and CO_2. When pyrolysis is performed under vacuum conditions, CO_2 and hydrogen concentrations in the product gas increase and CO amount decreases.

Bio-oil is a very complex mixture of oxygenated compounds, so in order to simplify the results products have been grouped taking into account their functional groups. The main pyrolysis products are phenols, which yield increases when working under vacuum conditions. At low pressure benzenediols amount is increased while guaiacols and alkyl-phenols decrease. On the other hand, one of the most interesting products in the bio-oil is levoglucosane, and its yield is augmented under vacuum conditions.

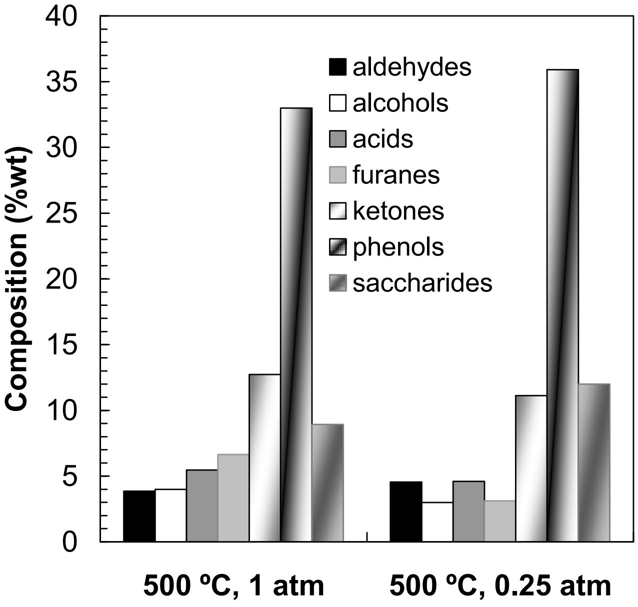


Figure 2. Effect of pressure in the composition of bio-oil.

Finally, biomass char has been characterized as well, due to its possible application as active carbon after being subjected to an activation process. It has been noticed that when operating at low pressure the surface properties of the char are improved.

References

[1]. Lopez G., Aguado R., Olazar M., Arabiourrutia M., Bilbao J., *Waste Management* **2009**, 29, 2649.

[2]. Aguado R., Olazar M., San Jose M.J., Aguirre G., Bilbao J., *Industrial & Engineering Chemistry Research*, **2000**, 39, 1925.

OP-III-A-5

PYROLYSIS OF HDPE IN A CONICAL SPOUTED BED REACTOR

Elordi G., Artetxe M., Lopez G., Amutio M., Aguado R., Olazar M.

University of the Basque Country,P.O. Box 644, 48080 Bilbao, Spain,
gorka.elordi@ehu.es

The production and use of plastics are increasing considerably, about 4% per year, due to their contribution to all daily activities. Thus, 5 million tonnes of high density polyethylene were produced in Western Europe in 2007 [1]. At present, only a small percentage of plastic waste is recovered or recycled, less than 20%. Pyrolysis is an alternative process for converting and upgrading plastic wastes. Pyrolysis in a fluidized bed reactor and similar devices has many possibilities for large-scale implementation of continuous waste plastic valorization [2]. The conical spouted bed reactor (CSBR) has interesting conditions for pyrolysis because of the low segregation in the bed and lower attrition than the bubbling fluidized bed. Furthermore, the CSBR has great versatility in the gas residence time, which may be reduced to values near 20 ms [3].

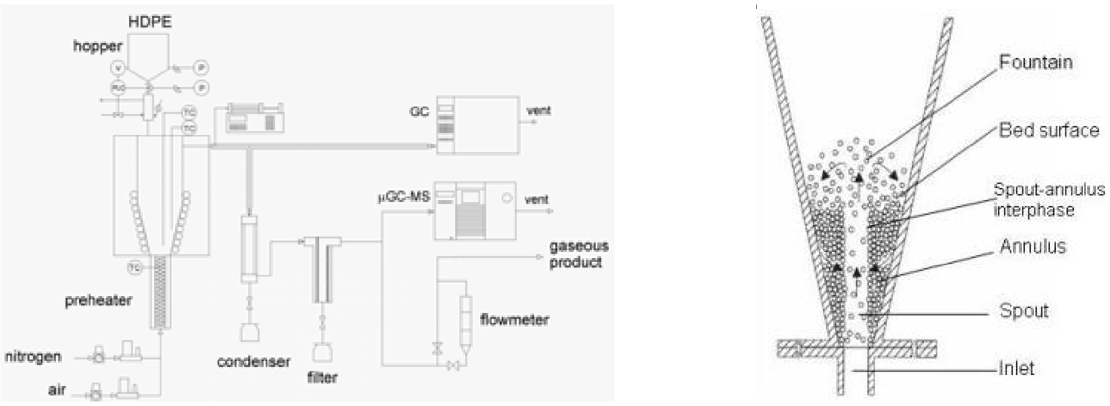


Figure 1. Schematic representation of the pirolysis unit; the CSBR in detail.

Batch runs have been carried out at 550, 600 and 650 °C. The bed consists of 100 g of sand ($0.6 < d_p < 1.2$ mm), and batches of 3 g of plastic (2 mm particle size) are fed into the reactor. The nitrogen flowrate is 20 % over that required for minimum spouting velocity (23 L min^{-1} at room conditions). Composition of products has been determined by GC analysis (Agilent 6890) of the reactor outlet stream at 10 s intervals during reactions. Weight loss and gaseous stream composition have been monitored throughout time. The calculation of product composition at a given time has been carried out using cyclohexane as the internal standard for mass balance closure, given that it is a product with insignificant yield and is easily identifiable.

Waxes have been collected in a set of filters controled by manual valves at different times and quantified by weight.

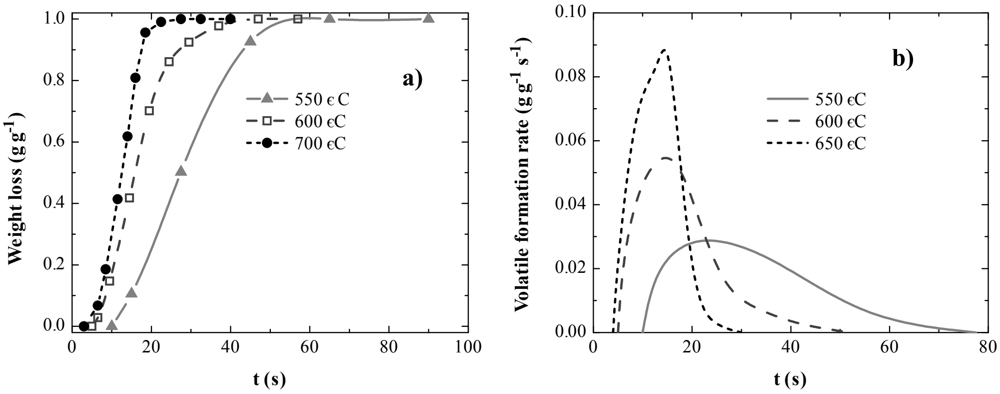


Figure 2. Polymer weight loss (a) and volatile formation rate (b).

Figure 2 shows the good performance of the reactor for this process. Due to the low conductivity of the polymer fed as pellets, the reaction begins after 10 s at 550 °C, whereas this initial period is shortened to 6 and 4 s at 600 and 650 °C, respectively. However, high heat transfer rates between phases in the CSBR avoid defluidization problems, which are common in fluidized bed reactors [4]. The polymer uniformly coats the sand particles thanks to their cyclic movement. The vigorous solid flow and the action of the spout avoid the formation of agglomerates and the reaction rate increases very fast once the polymer has been melted. Temperature has a great influence on reaction rate. Thus, at 550 °C the reaction finishes at around 70 s and volatile formation rate peaks around 30 s; at 600 °C, the reaction finishes at around 50 s and the maximum rate is located at 18 s, whereas at 650 °C these values correspond to 30 and 13 s, respectively. The wax fractions prevails at 550 and 600 °C, accounting for 60 and 49 wt% in each case. At 650 °C, diesel fraction components are the main lump (35 wt%), followed by the wax and gasoline fractions (25 wt%).

The simple design of a CSBR makes its scaling-up straightforward. Furthermore, its throughput by reactor volume unit is higher than that of a bubbling fluidized bed due to the lower amount of solid (sand) required for fluidization enhancement.

References

[1]. Plastics Europe’s Annual Report, Plastics Europe, Association of Plastic Manufacturers, 2007, p.26.

[2]. Kaminsky, W.; Predel, M.; Sadiki, A. *Polym. Degrad. Stab.* **2004**, *85*, 1045-1050.

[3]. Olazar, M.; San Jose, M.J.; Aguado, R.; Gaisan, B. *Ind. Eng. Chem. Res.* **1999**, *38*, 4120.

[4]. Arena, U.; Mastellone, M.L. *Chem. Eng. Sci.* **2000**, *55*, 2849.

REACTORS FOR THE GREEN TRANSFORMATION OF VEGETABLE OILS INTO FATTY ACID METHYL ESTERS (FAME) VIA BASED-CATALYSED TRANSESTERIFICATION WITH MINIMUM ENERGY INPUT

Barr G., Sermon P.A., Worsley M., Cheng Y. and Tuzun U.

Chemistry, FHMS and Chemical Engineering, FEPS, U niversity of Surrey, Guildford, Surrey, GU2 7XH, UK

The base-catalysed transesterification of sunflower oil has long been studied as a route to biofuels. Here the reaction with CH_3OH (9:1 molar ratio) at 333-298K has been promoted by 1wt% catalyst relative to the sunflower oil: NaOH (with H_3PO_4 neutralisation), CaO and CaO/C. Product analysis was in terms of the intensity ratio of ^{1}H resonances seen at 3.5-3.6ppm/2.3ppm by NMR in $CDCl_3$.

Traditionally, NaOH is an effective catalyst (see Figure 1), but requires subsequent H_3PO_4 neutralisation.

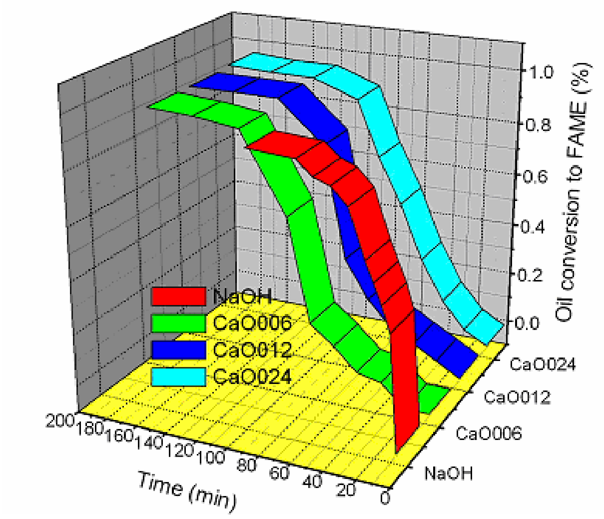
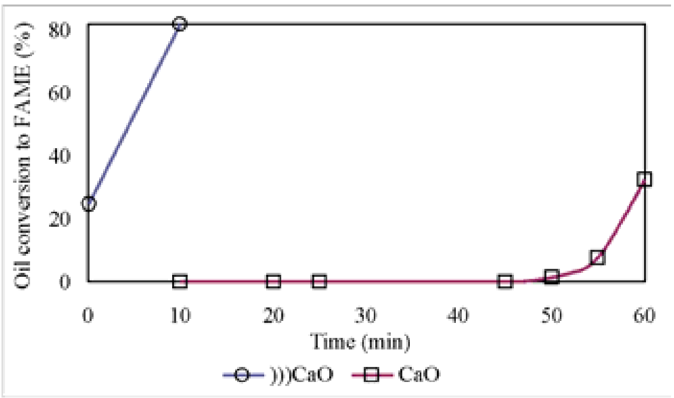
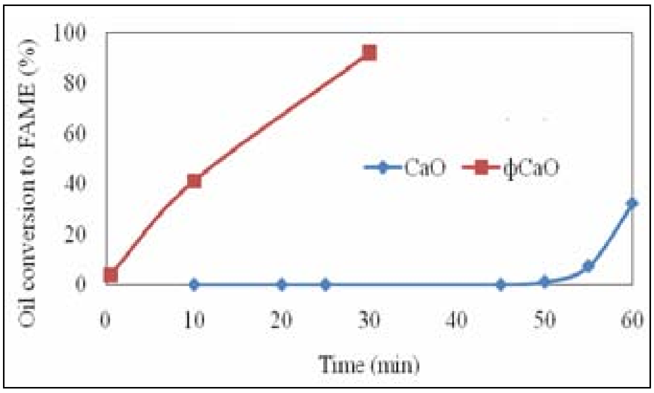


Figure 1. Sunflower oil conversion to FAME on NaOH and CaO catalysts at 333K.

It is found (see Figure 1) that, although CaO and CaO/C are more environmentally-friendly catalysts and do not require subsequent neutralisation, they are less effective than NaOH. However, the activity of the CaO-catalysed reaction is very effectively enhanced by ultrasonic agitation ***)))*** (see Figure 2a). Ultrasonic effects are known [A.P.Vyas, J.L.Verma and N.Subrahmanyam *Fuel* **89**,1-9,(2010)], but are energy intensive. Surprisingly, addition of 1% water again was found to *accelerate* the reaction (see Figure 2b); surprisingly, this did not appear to raise the level of free fatty acids. The reasons are considered.



a



b

Figure 2. (a) ^{1}H NMR deduced rate of transesterification of sunflower oil at 298K for ultrasonically- assisted (open circles: *))))*) reaction and mechanically-agitated (open squares). (b) Conversion of sunflower oil to FAME for CaO (blue) accelerated by the addition of water (red)

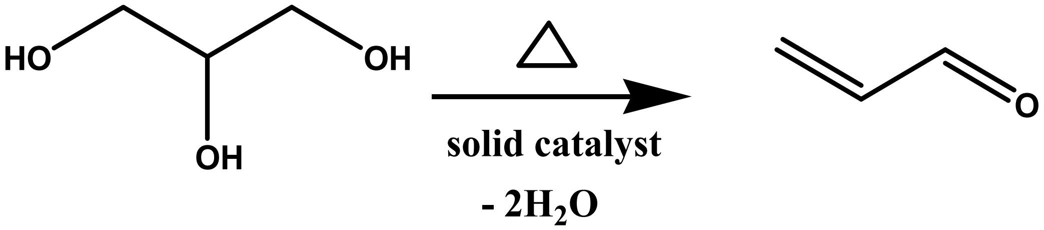
We report for the first time that the greenest and least energy intensive route to fatty acid methyl esters uses processing in nanoengineered thin film bubble reactors [W. Duangsuwan, U. Tuzun and P.A. Sermon *Chem. Eng. Sci.* **64**, 3147-3158, (2009)]. This approach maximises the rate of CH_3OH-transfer into the sunflower oil and sunflower oil into the methanol-catalyst suspension. The implications for such green reactors for the green processing of vegetable oils to biodiesel and the recycling of used cooking oil are also considered in detail.

DEHYDRATION OF GLYCEROL TO ACROLEIN

**<u>Haider M.H.</u>, Dummer N.F., Miedziak P., Taylor S.H., Willock D.,
Knight D.W., Hutchings G.J.**

*Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Wales, UK,
CF10 3AT, haidermh@cardiff.ac.uk*

Glycerol can be converted into many valuable products which act as intermediates for the synthesis of industrially important chemicals [1]. Moreover, its ready availability as a major by-product from the production of bio-diesel has made it attractive [3,4]. Acrolein is one of the products from glycerol dehydration [5]. This process has tremendous industrial applications in the manufacture of chemicals like acrylic acid esters, super absorber polymer production, detergents [5-9]. In the present work, comparison between different catalysts has been made in order to determine which characteristics impart high selectivity towards acrolein.



Dehydration of glycerol to acrolein (scheme 1) was carried out in a fixed bed flow reactor at the gas solid interface. Vaporisation of glycerol (0.5 wt% in water, 1 ml/h) occurred in a pre-heater, which was kept constant at 290°C while that of the catalytic reactor was changed over the range of 175 - 400°C, in order to see the change in selectivity towards acrolein. The experiments were run in an inert atmosphere of helium at a flow of 100 ml/min. Products were collected in water trap cooled with ice/water, followed by a liquid nitrogen trap to ensure complete recovery of liquid products. The analysis was conducted off line with Varian CP 3800 gas chromatograph equipped with capillary column (i.d. 0.53 X 30m).

Various acid catalysts were prepared and evaluated at different temperatures. The best performing catalyst gave 92mole % selectivity towards acrolein at a temperature of 220°C. Glycerol conversion was 100% with a carbon mass balance of 100%, giving a space time yield of 4.61X10^{-3} Kg$_{\text{Acrolein}}$m^{-3}$_{\text{catalyst}}$S^{-1}.

Figure 1 shows the schematic diagram of reactor setup with a syringe pump injecting glycerol/H_2O feed into the middle of the preheater through a long needle. The incoming gas, briefly heated to 180°C flows over the injector needle in the pre-heater, held at 290°C in order to ensure complete gasification of the feed. The temperature of the whole system is kept constant with the exception of the catalytic reactor which was varied between 200°C - 400°C.

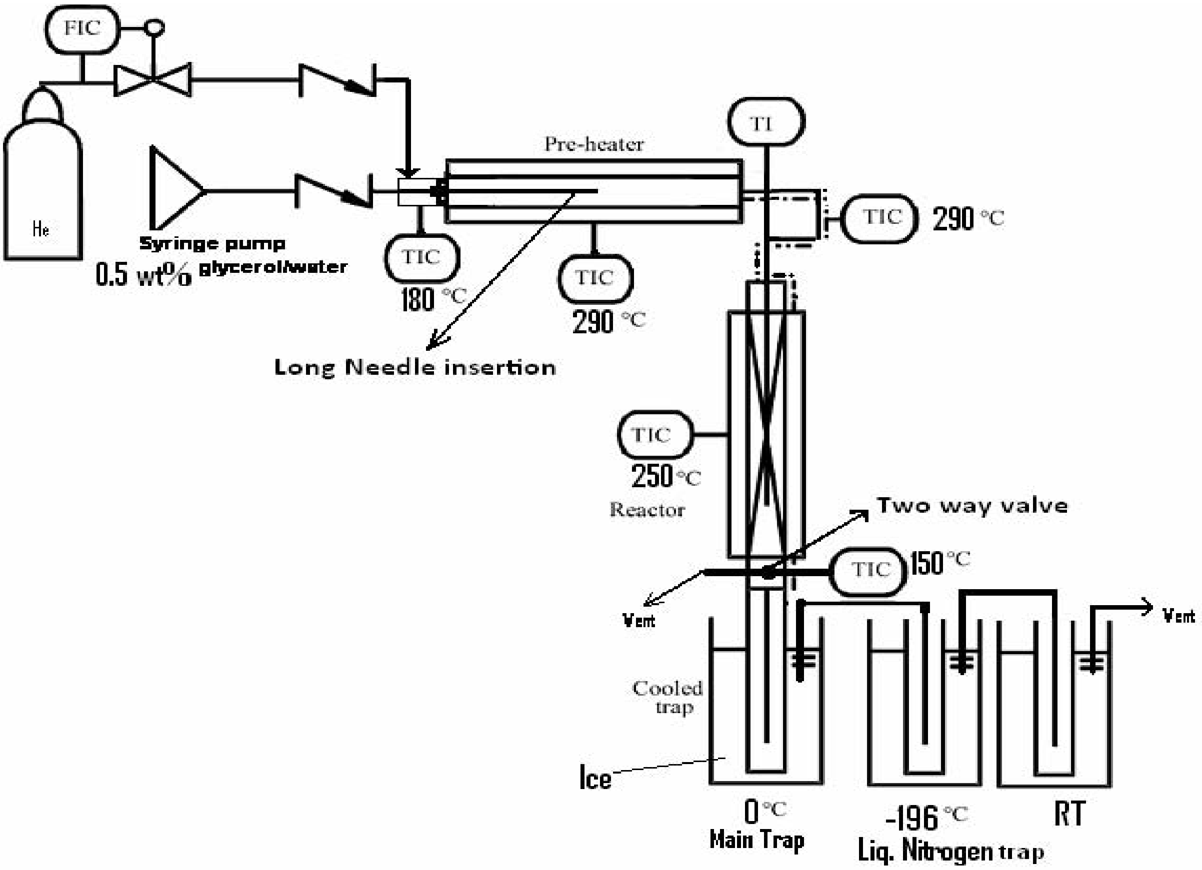


Figure 1 Schematic diagram of reactor setup.

References

[1] Klass D.L. (1998) Biomass for renewable energy, fuels and chemicals, Academic, San Diego, p 1.
[2] G. Centi, S. Perathoner (2003) Catal. Today 77:287.
[3] H. Van Bekkum, P. Gallezot (2004) Top Catal. 27:1.
[4] G.W. Huber, J.A. Dumesic (2006) Catal Today 111:119.
[5] H. Adkins, W.H. Hartung (1941) Org. Synth. Coll. 1:15.
[6] A. Neher, T. Haas, D. Arntz, H. Klenk, W. Girke (1995) U.S. Patent 5,387,720.
[7] E. Schwenk, M. Gehrke, F. Aichner (1933) U.S. Patent 1,916,743.
[8] S. Ramayya, A. Brittain, C. DeAlmeida, W. Mok, M.J. Antal (1987) Fuel 66:1364.
[9] L. Ott, M. Bicker, H. Vogel (2006) Green Chem., 8:214.
[10] Song Hai-Chai, Hao-Peng Wang, Bo-Qing Xu (**2009**) Applied Catalysis A: General 353: 213–222.

LACTIC ACID BASED ON BIO RESOURCES AS AN INTERMEDIATE FOR A SERIES OF THE MAIN CHEMICALS PRODUCTION

Kolbakov V.V.[1], Kozlovskiy R.A.[2], Parmon V.N.[3], Shvets V.F.[2]

[1]Nordbiochem Ltd., Põlva, Estonia, vambola@nordbiochem.com, +372-799-4811
[2]D. Mendeleyev University of Chemical Technology of Russia, Moscow, Russia,
RAKozlovskiy@mail.ru, +7-499-978-9554, shvets@muctr.ru, +7-499-978-9589
[3]Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia,
parmon@catalysis.ru +7-383-330-8269

The increasing cost of fossil fuels, development of new industry of motor fuel production from renewable sources and extraordinary growth of petrochemicals production in Asia force chemical industry to reconsider its traditional feedstock looking at alternative sustainable sources based on biomass. One of the examples of using of renewable sources for chemicals production is ethylene and polyethylene production through ethanol received from sugars. This process was realized in large scale by Dow Chemical Co in Brazil.

But the production of bioethanol, as a final product or intermediate, is not the best way of using of carbohydrates as renewable sources because of two molecules of waste carbon dioxide, formed per each molecule of glucose. Much more profitable way is production of lactic acid from carbohydrates. The yield of lactic acid (by weight) in this case is quantitative and the structure of lactic acid is very convenient for further using as a background chemical for syntheses of a lot of other products for chemical and farm industries. These products are polylactic acid (PLA), propylene glycol (PG), propylene oxide (PO), alkyl lactates (AL), pyruvic acid, acrylates and so on. All these products will be competitive with the corresponding petrochemicals in the case of low production cost of microbiological transformation of glucose to lactic acid.

We have developed very productive and economically attractive cell recycling process of lactic acid production from glucose. Microbiological transformation of glucose to lactic acid proceeds with a quantitative atom selectivity and quantitative yield. Existing process realized by Dow-Cargill six years ago includes batch fermentation process in huge size reactors. Duration of the process is more than 60 hours, biomass utilization is needed and isolation of pure lactic acid through calcium salts gives calcium sulfate wastes in the same quantity as lactic acid.

Our cell recycling process proceeds in a fermenter included in a recycling circuit with a membrane. Through this membrane final water solution of lactate ammonium removes from the system. Biomass in these conditions remains in the reactor and works as a catalyst. In these conditions there is no need to utilize biomass, there are no wastes of calcium sulfate and the specific productivity of the cell reactor is 20 times more than batch process.

Dow-Cargill earlier and Naturworks Company now use lactic acid produced in this batch process for biodegradable polymer production – polylactide.

Developing of new cell-recycling process essentially reduces operation cost and capital investments and make it possible to use lactic acid more widely as a background chemical for production of a series of large variety of chemical products. The self cost of lactic acid in our process is about 450 euro per ton.

The product of our fermentation process - ammonium lactate is used for butyl lactate synthesis with a recycle of ammonia to the fermentation stage. Butyl lactate received from ammonium lactate is a starting material for further catalytic synthesis of pure lactic acid, other lactic acid esters, propylene glycol, acrylates and polylactic acid.

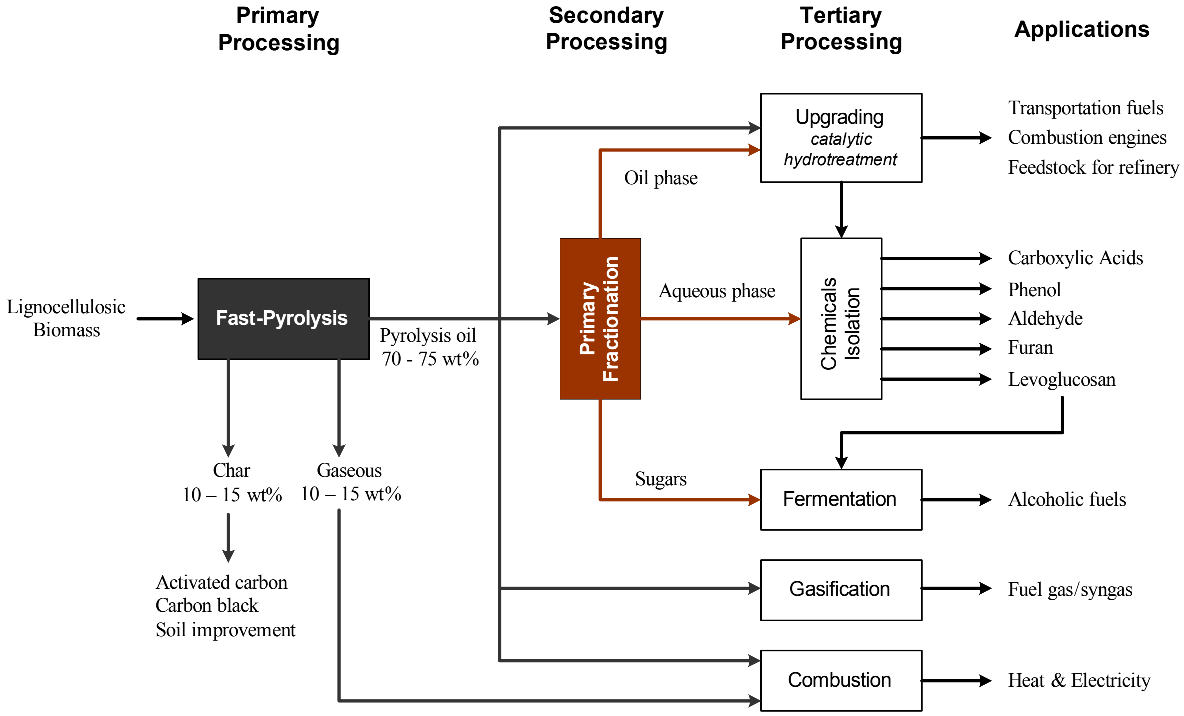
Low production cost of starting butyl lactate makes it possible to produce AL, PG, PO, PLA and other products with a competitive and low production cost.

RECOVERY OF ACETIC ACID FROM PYROLYSIS OIL BY REACTIVE EXTRACTION

Rasrendra C.B.[1], Girisuta B.[1], Winkelman J.G.M.[1], Leijenhorst E.J.[2], Venderbosch R.H.[2], Windt M.[3], Meier D.[3], Heeres H.J.[1]

[1]*Chemical Engineering Department, University of Groningen,*
Nijenborg 4 9747 AG Groningen, the Netherlands, h.j.heeres@rug.nl
[2]*BTG Biomass Technology Group B.V., Josink Esweg 34 7545 PN Enschede, the Netherlands*
[3]*vTI-Institute of Wood Technology and Wood Biology, Leuschnerstr. 91 D-2103 Hamburg, Germany*

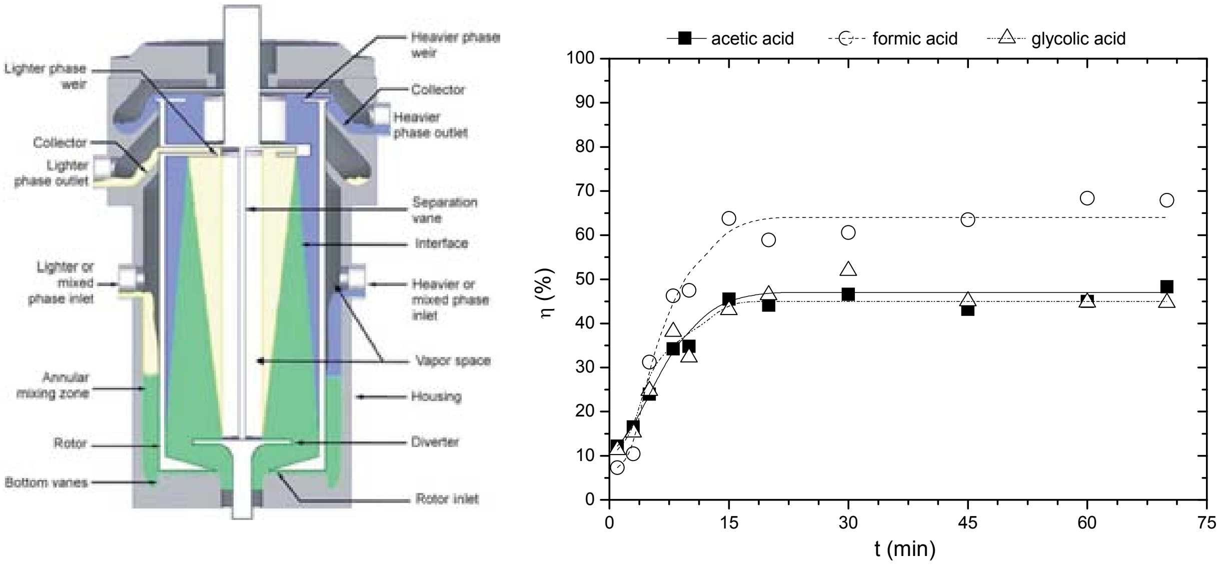
Fast pyrolysis oil is a very attractive feedstock for the production of high added value biobased chemicals, bio-fuels and energy using the biorefinery concept (Scheme 1).



Scheme 1. Biorefinery unit based on fast-pyrolysis of lignocellulosic biomass

An interesting high added value bulk-chemical from pyrolysis oil is acetic acid. It is the major organic acid in fast pyrolysis oil with concentrations of up to 10 wt%, depending to the feedstock and process conditions [1]. Generally, reactive extraction is an attractive recovery technology for organic acids [2]. However, in previous studies we have shown that the isolation of acetic acid from crude fast pyrolysis oil by reactive extraction with tertiary amines is cumbersome due to a relatively high solubility of the extractant in the pyrolysis oil [3]. A better solution is to isolate the organic acids not from the pyrolysis oil, but from aqueous streams available within the biorefinery scheme. A potentially attractive feedstock is the aqueous stream obtained from washing the pyrolysis oil with water. The organic acids tend to accumulate in the aqueous phase and as such this phase is better suitable for reactive extractions with a tertiary amine. The remaining oil phase may be processed further for bio-fuel and energy generation (Scheme 1).

Here, we report on the isolation of acetic acid from the aqueous stream of phase splitted pyrolysis oil by reactive extraction using a long chain aliphatic tertiary amine. Acetic acid recovery was optimised by selecting the proper amine and diluent combination and adjustment of the process conditions. The best results were obtained with tri-*n*-octylamine (TOA) in 2-ethyl-hexanol (86% acetic acid recovery at equilibrium conditions). The data were modeled using an equilibrium approach. The reactive extraction process was succesfully demonstrated using a bench scale continuous contactor-separator (CCS) (scheme 2) where acetic acid recoveries of 50% were obtained (Scheme 2).



Scheme 2. Continuous reactive extraction of acetic acid in the CCS device

References

[1] K. Sipilä, E. Kuoppala, L. Fagernäs and A. Oasmaa, Biomass and Bioenergy, 14 (1998) 103-113.
[2] A.S. Kertes and C.J. King, Biotechnology and Bioengineering, 28 (1986) 269-282.
[3] F.H. Mahfud, F.P. Van Geel, R.H. Venderbosch and H.J. Heeres, Separation Science and Technology, 43 (2008) 3056-3074.

Acknowledgements

Financial support from the EU Project BIOCOUP 518312 is gratefully acknowledged.

OP-III-A-10

LIPASE-CATALYZED REACTION IN A DOWN FLOW CONTINUOUS REACTOR IN ORGANIC SOLVENTS

<u>Serap Sahin</u>, Päivi Mäki-Arvela, Kari Eränen,Tapio Salmi, Dmitry Yu. Murzin

Process Chemistry Center, Åbo Akademi University, Turku, FI-20500, Finland;
E-mail: ssahin@abo.fi

Utilization of cascade methodology in which the intermediate product is converted in the forthcoming consecutive reactions without any separation in the same pot [1] has great potential for use in chemical industry. Enzymatic reactions can be favored over chemical catalysis due to the fact that enzymes display high enantioselectivity [2]. The vast majority of the enzymatic processes was performed in a batch mode [3-5]. However, there are only a few examples of processes carried out in continuous flow systems. The aim of this work was to study the kinetic resolution (KR) of racemic 1-phenylethanol (*R/S*)-**1** (Fig 1b) in a continuous flow reactor (Fig 1a).

The KR of (*R/S*)-**1** with ethyl acetate was performed in a down flow continuous reactor. The internal diameter and the length of the reactor are 1 cm and 12 cm, respectively. The reactor was filled with 3.5 cm quartz sand (> 355 μm) from the bottom on top of a 1 cm quartz wool layer. The catalyst bed containing a mixture of 0.125 g immobilized lipase, Novozym 435, and 1.5 g quartz sand had a height of 2.9 cm. The uppermost quartz layer which dimension is 3.5 cm in length distributes the liquid flow above the catalyst bed. The KR of (*R/S*)-**1** with ethyl acetate at the molar ratio of 1:3 in 400 mL toluene was perfomed at 70 °C. The solution was saturated with argon proir pumping into the reactor. The liquid flow rate was varied in a range of 1.5 mL min^{-1}-3 mL min^{-1}. The immobilized lipase was kept at 4 °C overnight between the experiments.

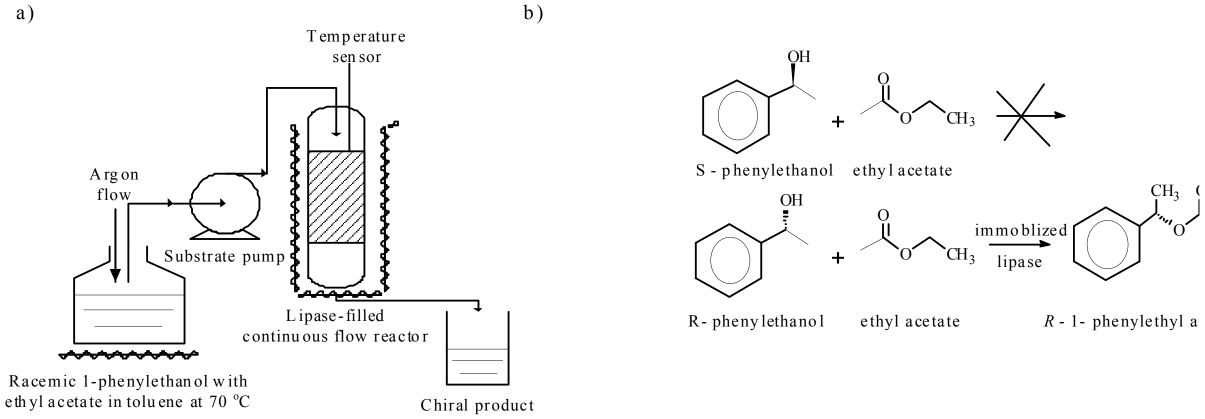


Figure 1. a) Simplified illustration of the experimental apparatus (~~: temperature control unit), b) enantioselective enzymatic esterification of *R*-phenylethanol with ethyl acetate as acyl donor.

OP-III-A-10

The results showed that increasing residence time (t=V/$\dot{V}$, where *V* is the catalyst bed volume and $\dot{V}$ is the volumetric flow rate of the liquid, respectively) from 45 s to 90 s doubled *R*-1-phenylethanol conversion (Fig 2). The conversion was decreased after 430 min when the reactant concentration was doubled. After 800 min the conversion was doubled as expected, due to the decreased volumetric flow rate to the half (Fig 2). No deactivation of the immobilized lipase was observed. The selectivity of *R*-1-phenylethyl acetate was 100 %.

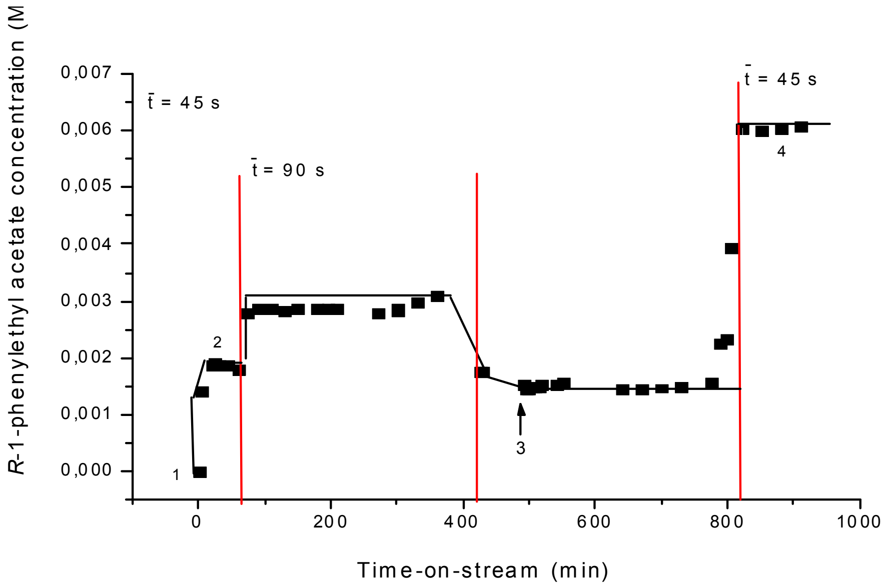


Figure 2. Kinetic resolution of (*R/S*)-**1** at 70 °C. Notation: 1; start-up of the first experiment using $\dot{V}$ =3 mL min^{-1}, 2; start-up of the second experiment using $\dot{V}$ =3 mL min^{-1} till 430 min time-on-stream, 3; start-up of the third experiment by doubling the reactant concentration using $\dot{V}$=3 mL min^{-1} till 810 min time-on-stream.Thereafter $\dot{V}$ =1.5 mL min^{-1} was applied.

The utilization of the continuous flow reactor for the kinetic resolution of racemic 1-phenylethanol with ethyl acetate in toluene over an immobilized lipase was successfully demonstrated in this study. In the final presentation transient kinetics, the effect of temperature and different solvents by applying step changes will be demonstrated. The comparison between the continuous flow reactor and the batch reactor modes for the kinetic resolution of racemic 1-phenylethanol will be discussed.

References

[1] Bruggink, A; Schoevaart, R; Kieboom, T. Org. Proc. Res. Dev. (**2003**), 7, 622–640.

[2] Jeong, S; Hwang, B-Y; Kim, J; Kim, B-G. J. Mol. Catal. B: Enzymatic (**2000**), 10, 597-604.

[3] Faber, K. Biotransformations In Organic Chemistry, 4th ed., Springer, Berlin, **2004**.

[4] Poppe, L; Novak, L. Selective Biocatalysis: A Synthetic Approach, VCH: Weinheim-New York, **1992**.

[5] Bornschauer, U T; Kazlauskas, R J. Hydrolysis In Organic Synthesis: Regio- and Stereoselective Biotransformation, Wiley-VCH, Weinheim-New York, **2006**.

OP-III-A-11

INVESTIGATION ON THERMOCHEMICAL CONVERSION OF PELLETIZED JATROPHA RESIDUE AND GLYCEROL WASTE USING SINGLE PARTICLE REACTIVITY TECHNIQUE

Atong D.[1], **Soongprasit K.**[2], **and Sricharoenchaikul V.**[3]

[1]*National Metal and Materials Technology Center, Thailand science Park,*
Pathumthani, 12120, Thailand
[2]*Department of Materials Science, Faculty of Science, Chulalongkorn University,*
Pathumwan, Bangkok, Thailand, 10330, Thailand
[3]*Department of Environmental Engineering, Faculty of Engineering, Chulalongkorn*
University, Bangkok, 10330, Thailand, viboon.sr@chula.ac.th

Adverse environmental effects resulting from fossil fuel usage as well as foreseeable conventional energy depletion lead to the exploration of alternative fuel materials especially the renewable ones. In this work, characterization of synthetic fuel material formed by pelletization of Jatropha residue (physic nut) using glycerol waste as a binder was carried out in order to investigate the feasibility of utilizing these waste materials as another renewable energy source [1]. Both wastes are by products from biodiesel manufacturing process. Synthetic fuel materials of Jatropha residue mixed with 0-50% glycerol waste were formed to length of about 11 mm and diameter of about 13 mm under pressure of 7 MPa in a hydraulic press. Maximum compressive stress (2.52×105 N/m^2) of the fuel pellet occurred at 10% glycerol waste. Thermal conversion characteristic of solid fuel was studied by using single particle reactivity testing scheme at temperature of 500-900°C under partial oxidation atmosphere As shown in Figure 1.

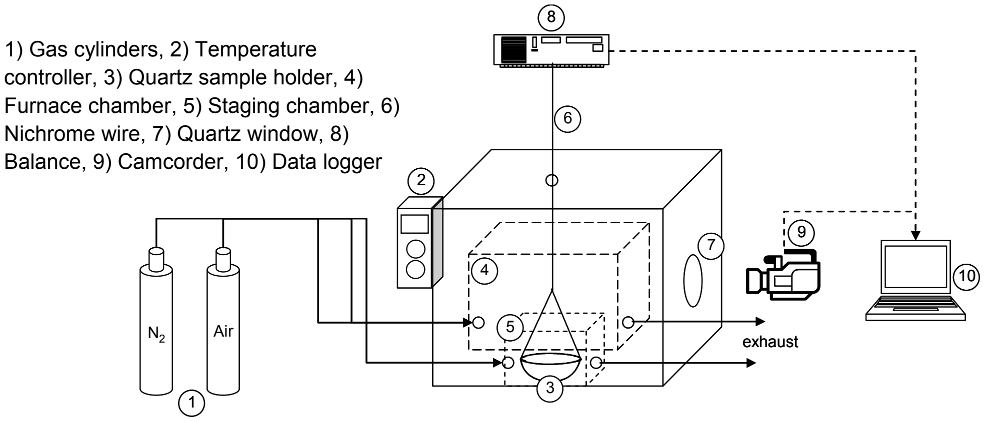

1) Gas cylinders, 2) Temperature controller, 3) Quartz sample holder, 4) Furnace chamber, 5) Staging chamber, 6) Nichrome wire, 7) Quartz window, 8) Balance, 9) Camcorder, 10) Data logger

Fig. 1 Schematic of single particle reactivity testing apparatus.

In general, higher glycerol content in solid fuel as well as oxygen concentration in reacting gas resulted in greater decomposition rate from 0.006-0.110 g/sec. Burning started with a relative short drying phase, followed with a longer pyrolysis time and thereafter the dominated char combustion time which took around 35-57% of total conversion time (Figure 2). The average total conversion time varied from 26 to 288 sec, depended mainly on reaction temperature. Higher glycerol content resulted in char with lower density and higher shrinkage with greater porosity. Greatest changes in pellet diameter, height, and density of 75.6%, 89.2%, and 91.5%, respectively, were exhibited at 5% oxygen atmosphere and 900°C.

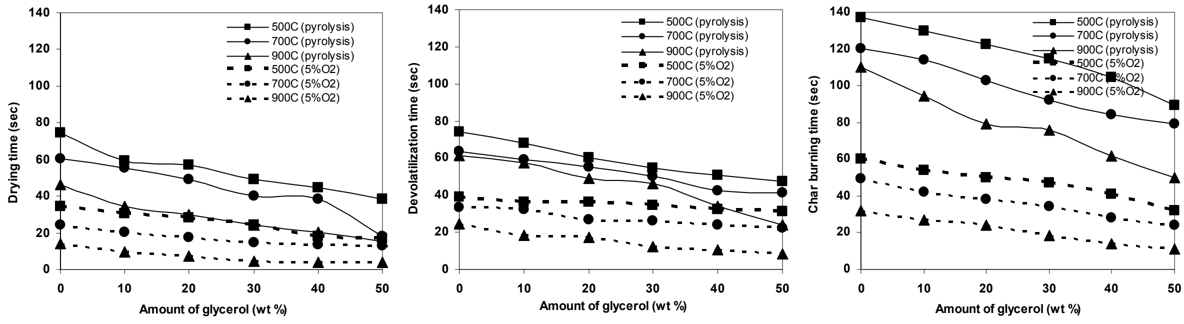


Fig. 2 Effect of glycerol content, temperature, and oxygen content on the duration of (a) drying, (b) devolatilization, and (c) char burning time

The SEM images of chars at different composition (Figure 3) indicated the existence of little pores in sample with smaller amount of glycerol (10 wt%). Surface morphological changes were evident after 900°C of pyrolysis. Porous structure seemed to be counteracted by the molten layer which indicated that sample may face with sintering problem at this high treatment temperature. Sample burned in the presence of oxygen atmosphere yield char sample with higher degree of porous structure. The results suggested that Jatropha residue mixed with glycerol is suitable for utilization as quality solid fuel.

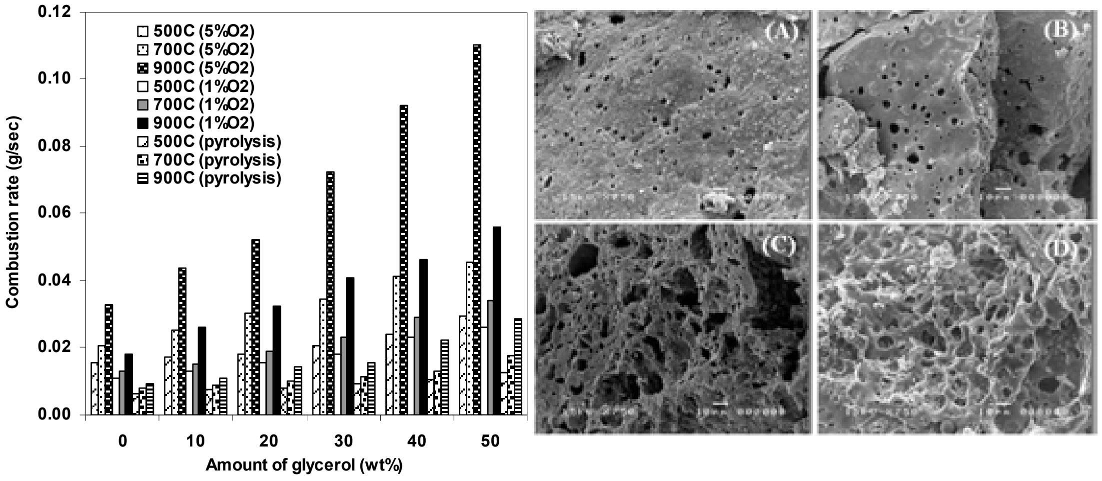


Fig. 3 Combustion rate and SEM images of chars (a) pyrolysis at 500°C, (b) 10wt% glycerol pyrolysed at 500°C, (c) 50wt% glycerol pyrolysed at 500°C, (d) 50wt% glycerol pyrolysed at 900°C

Reference

[1]. Chaudhari, S.T. and Bakhshi, N.N., Report Bioenergy Development Program renewable Energy Branch, Energy, Mines and resources Canada, February, 2002, 396-436.

SELECTIVE CATALYTIC DEOXYGENATION OF FATTY ACIDS AND THEIR DERIVATIVES; CATALYST DEACTIVATION, REACTOR SELECTION AND MODELLING

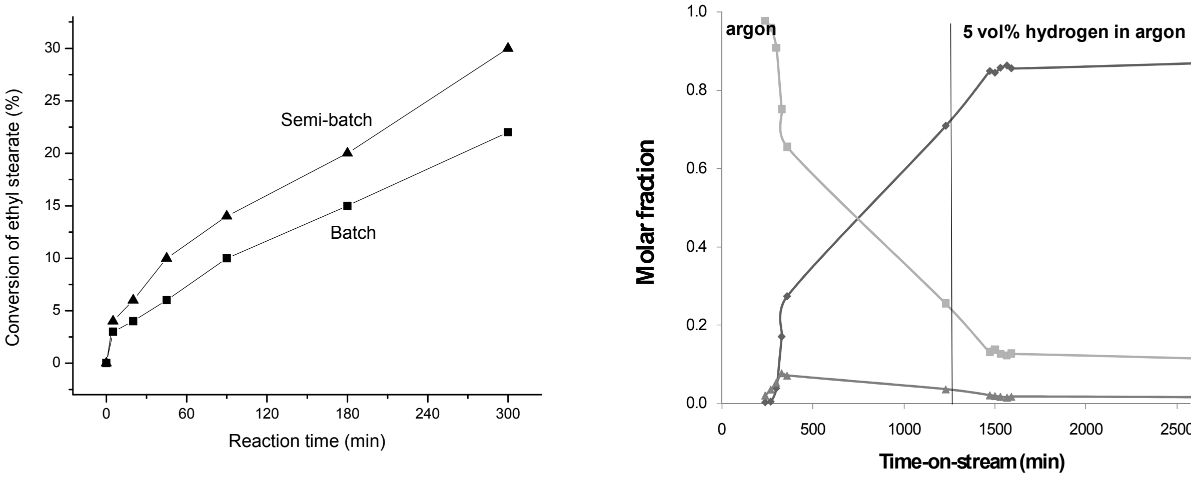
Päivi Mäki-Arvela, Teuvo Kilpiö, Tapio Salmi, Dmitry Yu. Murzin

Process Chemistry Centre, Åbo Akademi University, FI-20500 Turku, Finland

Selective catalytic deoxygenation of fatty acids and their derivatives has been demonstrated over Pd/C and Pt/C catalysts. In case of stearic acid as a substrate, the main liquid phase product was n-heptadecane but small amounts of n-heptadecene were formed. The deoxygenation of the corresponding ester, ethyl stearate proceeded via formation of stearic acid as an intermediate. CO and CO_2 were the main gaseous products in both cases. These gaseous products could partially deactivate the catalyst and thus the selection of the reactor type is of crucial importance in prolonging the catalyst life time. Furthermore, for the industrial applications, the continuous operation is a more attractive one, compared to the batch mode. The aim of this work was to compare the effect of different reactor types in catalytic deoxygenation of fatty acids and their derivatives. For this purpose batch, semibatch as well as two types of continuous reactors were applied.

Catalytic deoxygenation was performed in a temperature range of 270°C to 360°C under 6 – 17.5 bar total pressure either under Ar or 1 – 5 vol% H_2 in Ar. Both microporous active carbon as well as mesoporous synthetic carbon, Sibunit, were used as catalyst supports for Pd with the loading varying from 1 wt.% up to 5 wt%. The batch reactor was operated typically using 1 g of catalyst and varying the inital concentration of fatty acid (or ester) from 0.16 mol/l to 1.6 mol/l in dodecane. Diluted streams as well as neat stearic acid were used as a feedstock for the continuous reactor. When the same reactor was used in semibatch mode, the gas phase was flowing through the reactor. Furthermore, two types of fixed bed reactors were applied in this work, namely a fixed bed upflow reactor in the absence of flowing carrier gas as well as a downflow reactor together with a cocurrent gas flow.

The results revealed that the batch reactor gave lower conversions of ethyl stearate than achieved in the semibatch reactor (Fig. 1a). This result can be explained by the fact that the CO formed can be continuously purged from the catalyst surface with the aid of the carrier gas flow in the semibatch reactor.



a) b)

Fig. 1. a) Conversion of ethyl stearate as a function of the reaction time in batch and semibatch reactors by using the initial concentration of ethyl stearate 1.6 mol/l, 1 g of 5 wt.% Pd/C, temperature 300˚C, pressure 17 bar using 5 vol.% H_2 in Ar, b) Kinetics of the stearic acid deoxygenation in the trickle bed reactor over 1 wt.% Pd/C (Sibunit) at 360^{o}C and 10 bar; under Ar for the first 1350 min and thereafter under 5% H_2 in Ar. Notation: (◆) stearic acid, (■) n-heptadecane and (▲) n-heptadecene. The concentration of neat stearic acid was 4.4 mol/l, Ar flow was 10 ml/min and the reactant flow was 0.075 ml/min.

The continuous downflow trickle bed reactor together with the cocurrent carrier gas flow was applied for deoxygenation of neat stearic acid at 360°C under 10 bar of Ar over a mesoporous Pd/C(Sibunit). A stable conversion (17%) of stearic acid was achieved during 2700 min time-on-stream (Fig. 1b). In the final work, several case studies from catalytic deoxygenation of fatty acids from C12-C23 and their derivatives using different reactors, reactants and catalysts are discussed and the results from the reactor modeling and quantification of the catalyst deactivation will be presented.

ETHANOL STEAM REFORMING OVER COBALT TALC IN A PLATE MICROREACTOR

Domínguez M., Cristiano G., Roig M., López E., Llorca J.

Institut de Tècniques Energètiques, Universitat Politècnica de Catalunya
Av. Diagonal 647, Ed. ETSEIB, 08028 Barcelona, SPAIN
Fax: (0034)934017149, E-mail: jordi.llorca@upc.edu

Introduction

Ethanol steam reforming (ESR) is suited for the production of hydrogen in industrial environments as well as for on-board feeding of internal combustion engines and on-demand feeding of fuel cells in mobile applications. This topic has received increasing attention in recent years mainly due to the renewable character of bio-ethanol, its non-toxicity, low price, and easy production and transportation [1]. ESR is an endothermic reaction (ΔH^0~216 kJ/mol) that yields a maximum of 6 mol of H_2 per mol of ethanol, half of which originates from water: $C_2H_5OH + 3\ H_2O \rightarrow 6\ H_2 + 2\ CO_2$.

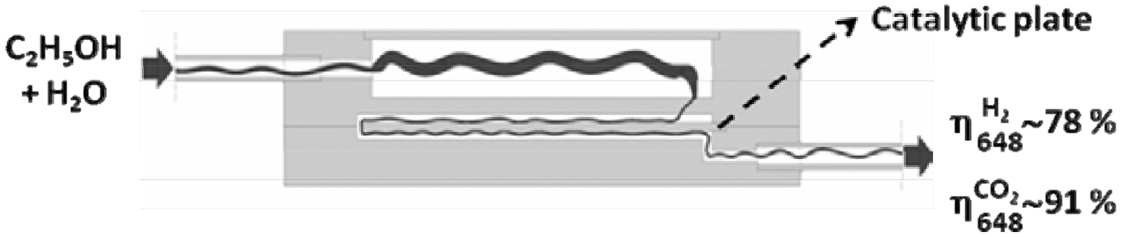
Traditionally, ESR has been studied over powdered catalysts in order to obtain a good catalyst formulation towards achieving high activity and H_2 selectively while operating at low reaction temperature and suppressing other side products, such as CO and CH_4 [2,3]. However, although much work has been addressed in that direction, powdered catalysts are not suited for industrial and mobile environments due to poor heat and mass transfer characteristics, elevated pressure drop and attrition problems, among others, and new reactor configurations need to be developed and tested for practical application [4]. In this work we have designed a stainless steel plate microreactor for performing ESR and tested it operating at short contact times. Moreover, we developed a method for coating plates with cobalt talc catalyst. We have used cobalt talc since it has been recently reported as one of the best catalysts for conducting ESR at low temperature and, in addition, it does not require any activation treatment after start up/shut down cycles [5].

Plate microreactor

A plate microreactor consisting of two stainless steel bodies was designed for hosting a stainless steel catalytic plate measuring 50x20x1 mm. A mixing and pre-heating chamber was included and bores were implemented to assure a uniform distribution of the feed. Both sides of the catalytic plates were covered with a well dispersed layer of cobalt talc with a thickness of about 0.5 μm. The deposition of the cobalt talc was accomplished by a novel hydrothermal route. Several hydrothermal conditions were explored by varying the temperature, time and concentration of precursors. Also, the effect of various pickling treatments on the adherence of the catalyst layer on the stainless steel plate was evaluated. The structure and composition of the different catalytic plates as well as their mechanical stability were studied by X-ray diffraction, scanning electron microscopy, reflectance infrared spectroscopy, confocal imaging and mechanical vibration techniques.

Catalytic tests

ESR was carried out at atmospheric pressure in the plate microreactor with a gaseous stream of 2.5-6.0 μmol/s C_2H_5OH (S/C=3) diluted in N_2. Reaction was performed at varying temperature (598-773 K), contact time (0.02-0.05 s), and catalyst loading (1-3 mg/cm^2).



Several reaction runs were carried out simulating start up/shut down cycles typical of a reforming reactor for mobile application. The microreactor showed a good dynamic behavior, fast response and reproducibility of hydrogen yield values. No pre-activation was required.

References

[1] Ledesma, C., Domínguez, M., Jiménez, N., López, E., Llorca, J. *Chem. Today*, **2009**, 27, 5, 40.
[2] Haryanto, A. Fernando, S. Murali, N. Adhikari, S. *Energy Fuels*, **2005**,19, 2098.
[3] Vaidya, P.D. Rodrigues, A.E. *Chem. Eng. J.*, **2006,** 117, 39.
[4] Casanovas, A., Domínguez, M., Ledesma, C., López, E., Llorca, J. *Catal. Today*, **2009**, 143, 32.
[5] Domínguez, M., Taboada, E., Molins, E., Llorca, J. *Catal. Today*, **2008**, 138, 193.

Acknowledgements

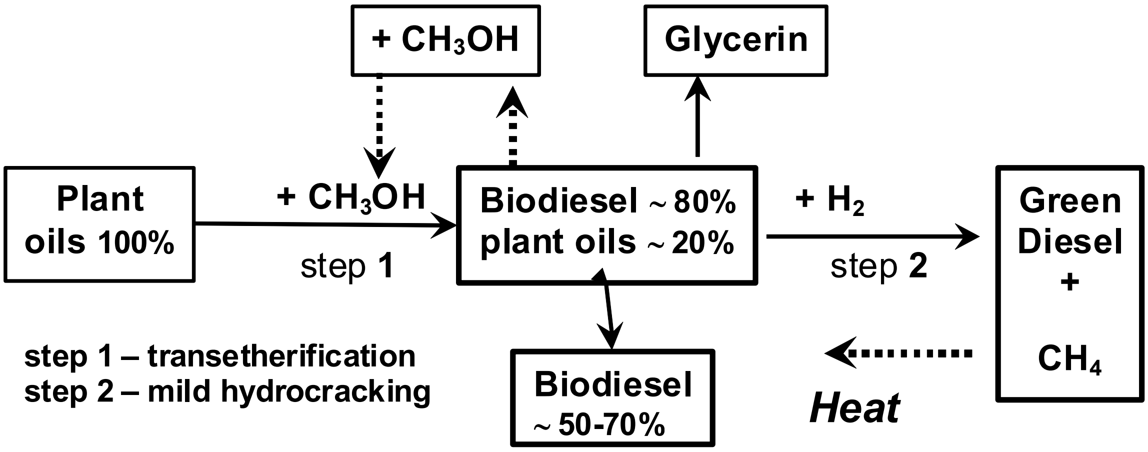
Financial support from MICINN through grant CTQ2009-12520 is acknowledged.

HYDROTREATMENT CATALYSTS DESIGN FOR BIO-FUELS PRODUCTION

Yakovlev V.A.[1], **Khromova S.A.**[1], **Bykova M.V.**[1], **Yermakov D.Yu.**[1],
Heeres H.J.[2], **Venderbosch R.H.**[3], **Parmon V.N.**[1]

[1]*Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia,*
E-mail: yakovlev@catalysis.ru
[2]*University of Groningen, Groningen, the Netherlands*
[3]*BTG Biomass Technology Group BV, Enschede, the Netherlands*

Biomass is a renewable alternative to fossil raw materials in the production of liquid fuels and chemicals. The objective of this work is to develop two-stage technology for biodiesel and green diesel production from lipidic renewables (plant oils, animal fats, algae lipids). The specificity of the work is development of new effective catalysts, adjusted to renewable feedstock. The technology is based on conjugated catalytic processes of transetherification and mild hydrocracking represented on the scheme below:



Main features of developed technology are:

- biofuel production of two types: biodiesel and green diesel;
- varying of biodiesel and green diesel yields depending needs;
- optimization of hydrogen consumption;
- energy-supply of both stages via burning of gaseous products, produced on 2nd step.

Catalytic characteristics of the technology include application of heterogeneous basic trasetherification catalysts under 200-220°C and 2.0 MPa and possibility of multiple catalyst regeneration for the first stage. For the second stage these ones comprise using of non-sulfided and non-noble metal catalysts, mild reaction conditions (300-340°C and 2.0 MPa H_2) and possibility of green diesel production with different cetane number via hydroisomerization catalysts application.

Thus, developed transetherification and mild hydrocracking processes allow to obtain high-clean biodiesel and green diesel with high cetane number, which can be used as improving additive to traditional fossil diesels. Developed new effective catalysts can be used in processing of non-food lipidic renewables.

ORAL PRESENTATIONS

SECTION III

Chemical Reactors and Technologies for Emerging Applications

Section III-B

Environmental Protection and Utilization of Wastes
Production of Hydrogen and Green Fuels
Advanced Processing of Natural Gas and Oil

OP-III-B-1

INVESTIGATION OF HYDROGEN PRODUCTION BY BIOMASS PARTIAL OXIDATION

Hanika J.[1], **LedererJ.**[2], **TukačV.**[3], **VeselýV.**[1]

[1]*Institute of Chemical Process Fundamentals, Czech Academy of Sciences, v.v.i.,*
165 02 Prague 6, Czech Republic, hanika@icpf.cas.cz, vesely@icpf.cas.cz,
[2]*VUANCH, a.s., Revoluční 84, 400 01 Ústí n. Labem, Czech Republic,*
jaromir.lederer@vuanch.cz,
[3]*Institute of Chemical Technology Prague, Technická 5, 166 28 Prague 6,*
Czech Republic, vratislav.tukac@vscht.cz

Keywords: *hydrogen, biomass, rape waste, partial oxidation*

Nowadays hydrogen demand caused by deep fuel refining and the other sustainable processes leads to utilization of new raw materials. Simultaneously, extensive biodiesel production creates great amount of biomass wastes transcendent over feeding potential of farm animals. One of potentially useful process of hydrogen production from renewable natural sources seems to be partial oxidation (POX) and gasification of biomass material like rape meal from rape oil production.

The goal of this work was to develop simulation model of experimental POX reactor working with rape meal and fuel oil mixture.

Experimental setup was constructed in pilot plant unit of UNIPETROL RPA consisted of water steam generator, continuous suspension batcher, gasification reactor equipped by co-annular feeding jet burner (see Figs. 1 and 2), water quench and heat exchanger.

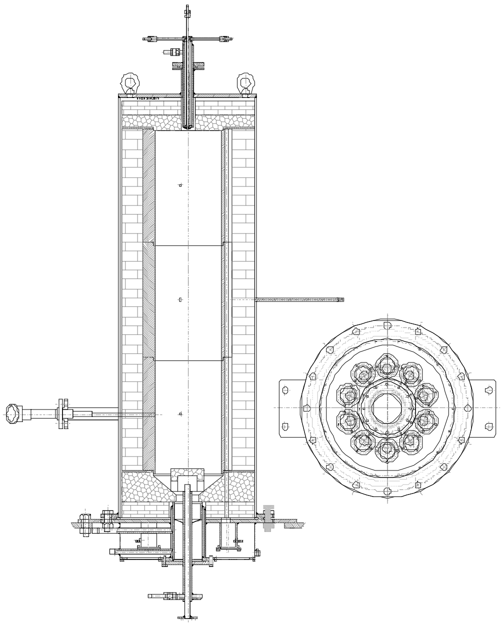


Fig.1: Pilot plant gasification reactor

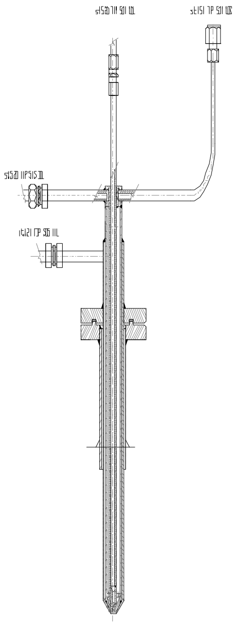


Fig. 2: Co-annular jet burner

Reactor parameters:

Internal diameter	0,3 m
Length	1,8 m
Volume	0,11 m^3
Working temperature	1000 - 1200°C
Under-pressure versus atmosphere	100 – 400 Pa
Internal co-annular jet	steam, oxygen
External co-annular jet	biomass dispersion in oil
Dispersion feed rate	1,5 – 3 kg/h
Oxygen flow rate	2 – 3 kg/h
Steam feed rate	1,25 kg/h

Distribution of residence time of biomass particles in the reactor affects results due to different rate of consecutive reaction steps: pyrolysis, water gas shift and steam reforming reactions. The following processes can be observed depending on temperature:

- Thermal dissociation of volatile components (473 – 553 K)
- Hydrocarbons formation/release (553 – 773 K)
- Cracking of biomass structure (773 – 973 K)
- Gasification of non-volatile components - soot reacts with oxygen and steam (973 – 1173 K)
- Thermodynamic equilibrium – preferential hydrogen and carbon monoxide formation (temperature above 1573 K)

Mathematical model developed in this study consists of two steps. First simulation model was created in process simulator Aspen Plus in form of pseudo-homogeneous CSTR to fit reaction kinetics and equilibrium on experimental data. Second CFD simulation model was developed in COSOL Multiphysics (PDE solver by finite element method) to find steady state gas velocity, temperature and concentration profiles inside of gasification reactor.

Complicated chemical composition was solved by concept of representative chemical compounds resulting in the same elemental composition as the original raw material. Instead of cellulose, lignin, proteins and phospholipids forming waste biomass similar compounds – glucose, vanillin, n-butyl-styrene, methionine and tri-ethyl-phosphate were applied for process simulation. For these compounds all necessary physicochemical data were available in the software database.

Hydrogen production depends both on oxygen and water steam ratio to biomass and hydrocarbon oil mixture and also on flow characteristics, temperature field and internal mixing in the reactor. Typical result of rape waste/hydrocarbons (1/10 wt/wt) mixture gasification during partial oxidation was as follows:

adiabatic temperature of product	1038 °C
hydrogen volume fraction	0.487
carbon monoxide volume fraction	0.358
molar ratio of CO / CO_2 of product	8,08

Distribution of residence time of biomass particles in the reactor affects results due to different rate of consecutive reaction steps: pyrolysis, water gas shift and steam reforming reactions. Qualitative agreement of experimental results with process simulation using AspenPlus simulator has been reached in this study. CFD modelling of the transfer phenomena inside the gasification reactor can help to understand complex phenomena in the reactor as well.

Acknowledgement

Project „BIOVODIK“, No. 2A-2TP1/024 , Program „Trvalá prosperita“, was supported by the Ministry of Industry and Trade of the Czech Republic.

References

[1]. T.A. Mihne, C.C. Elam and R.J. Evans, „Hydrogen from Biomass - State of the Art and Research Challenges“, A Report for the International Energy Agency Agreement on the Production and Utilization of Hydrogen Task 16, Hydrogen from Carbon-Containing Materials, 2002.

[2]. H. Haykiri-Acma, S. Yaman, „Interpretation of biomass gasification yields regarding temperature intervals under nitrogen-steam atmosphere“, Fuel Processing Technology 88 (2007) 417 – 425.

[3]. Institut Français du Pétrole: Fuels and Engines, TECHNIP Ed., Paris 1999.

[4]. Tukač V., Tomešová Z., Hanika J., Veselý V., Lederer J., Nečesaný F., Hydrogen production by partial oxidation of waste biomass, 18. Conference APROCHEM, Milovy 20.-22.4.2009, Proceedings Vol.1, pp.1140-1147T.A.

[5]. Aspen Plus User Guide, Aspen Technology Inc., 2001, Cambridge, USA.

[6]. Turpeinen E., Keiski R.L., Evaluation of hydrogen production from metallurgical flue gases using Aspen Plus simulation software, Book of Abstract ECCE 6, 1a, 623, abs.3073, Copenhagen, 16-20 Sept. 2007.

JOINT STEAM REFORMING OF BIO-OIL AND BIO-ETHANOL FOR HYDROGEN PRODUCTION

Remiro A., **Valle B.**, **Vicente J.**, **Gayubo A.G.**, **Bilbao J.**

Department of Chemical Engineering, University of the Basque Country.
P.O. Box 644, 48080 Bilbao, Basque Country, aingeru.remiro@ehu.es

Introduction

The catalytic steam reforming of biomass-derived oxygenates (such as the bio-oil obtained by fast pyrolysis or the bio-ethanol obtained by fermentation) is a promising alternative for hydrogen production that could contribute to developing the biorefinery concept [1]. The viability of bio-oil upgrading by catalytic processes, such as steam reforming, is restricted by the problem associated with the deposition of pyrolytic lignin (formed by the polymerization of phenol derivatives contained in the crude bio-oil) in the reactor and on the catalyst, which causes fast deactivation of the catalyst and equipment blockage [2]. Previous studies have proven that a thermal treatment step (for carrying out a controlled polymerization of bio-oil phenol-derived compounds) prior to the catalytic reactor [3] and the co-feeding of light alcohols [4] contribute to attenuating these problems.

The catalytic steam reforming of a bio-oil/bio-ethanol mixture is studied in this paper in a two-step process: thermal treatment + catalytic steam reforming. The effect of co-feeding ethanol with bio-oil on the amount of residual carbon deposited in the thermal treatment, H_2 yield, bio-oil conversion and catalyst stability have been analyzed in order to prove the viability of the overall process.

Experimental

The bio-oil (obtained from fast pyrolysis of pine sawdust) has been separated into two fractions (aqueous, 64 wt%, and organic, 36 wt%) by adding water with a mass ratio 2/1. The aqueous fraction is composed of 19 wt% organics ($CH_{1.80}O_{0.65}$) and water, which corresponds to a steam/carbon ratio, S/C=5.8. The addition of ethanol has been carried out by maintaining the S/C ratio constant and modifying the bio-oil/ethanol mass ratio (100/0, 80/20, 60/40, 40/60 and 0/100).

The reaction equipment consists of a two-unit system: a U-shaped steel tube is used for the thermal treatment (200 °C) of the feed, and steam reforming is subsequently carried out in a fluidized bed reactor. The kinetic runs (at 700 °C and with a space velocity of 42000 h^{-1}) have been carried out on a Ni/α-Al_2O_3 catalyst prepared by wet impregnation of the support with a nitrate solution of 10 wt% Ni. The catalyst (100-300 μm) was mixed with an inert solid (carborundum (37 μm) with a catalyst/inert mass ratio = 1/20) in order to improve the hydrodynamic properties of the catalytic bed. Before the reforming reaction, the catalyst was reduced at the reaction temperature for 2 h using H_2-He flow with a H_2 content of 11 vol %.

Results and discussion

Table 1 shows the percentage of residual carbonaceous product deposited during the thermal treatment (by mass unit of the bio-oil in the feed). It is observed that an increase in ethanol in the feed promotes a slightly smaller carbon deposition. Figure 1 shows the evolution with time on stream of the selectivity of H_2 (expressed as molar percentage of H_2 in the gaseous stream) during the steam reforming of bio-oil/ethanol mixtures. Initial H_2 selectivity increases and catalyst deactivation notably decreases for higher amounts of ethanol in the feed. The performance of a bio-oil/ethanol mixture with 40/60 mass ratio is very close to that of ethanol steam reforming.

Table 1. Residual carbonaceous product deposited in the thermal treatment at 200 °C for different bio-oil/ethanol mixtures.

Bio-oil/ethanol (wt%)	residual carbon (wt%)
100/0	33.4
80/20	32.7
60/40	27.6
40/60	26.8
0/100	0

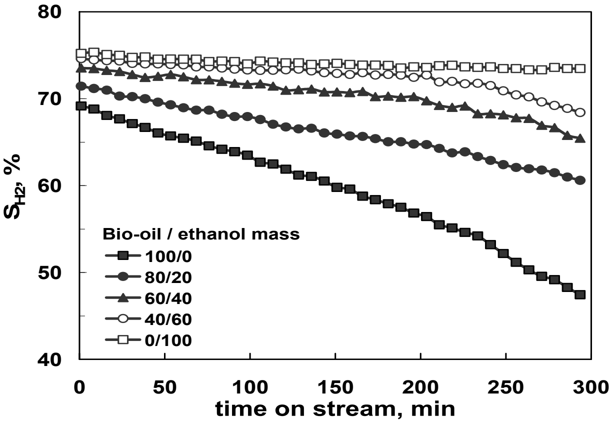


Figure 1. H_2 selectivity in bio-oil/ethanol steam reforming on a Ni/α-Al_2O_3 catalyst. Reaction conditions: 700 °C, S/C = 5.8. G_{C1}HSV= 42000 h^{-1}.

References

[1] Huber, G.W., Corma, A., *Angew. Chem. Int. Ed.*, **2007**,*46*, 7184-7201.

[2] Gayubo, A.G., Aguayo, A.T., Atutxa, A., Aguado, R., Olazar, M., Bilbao, J., *Ind. Eng. Chem. Res.*, **2004,** *43*, 2619-2626.

[3] Gayubo, A.G., Valle, B., Aguayo, A.T., Olazar, M., Bilbao, J., *J. Chem. Technol Biotechnol.*, **2010**, *85*, 132-144.

[4] Gayubo, A.G., Valle, B., Aguayo, A.T., Olazar, M., Bilbao, J., *Energy & Fuels*, **2009**, *23*, 4129-4136.

Acknowledgements

This work was carried out with the financial support of the Ministry of Science & Technology of the Spanish Government (Project CTQ2006-12006).

LANDFILL BIOGAS PURIFICATION FOR H_2 PRODUCTION

Hernandez S.[1], **Mescia D.**[2], **Chiappero M.**[3], **Russo N.**[3] **and Fino D.**[3]

[1]*Italian Institute of Technology, Center for Space Human Robotics (IIT@POLITO),*
Torino, Italy, simelys.hernandez@itt.it
[2]*Asja Ambiente Italia, Rivoli, Italy*
[3]*Department of Material Science and Chemical Engineering, Politecnico di Torino,*
Torino, Italy

The aim of this work, carried out on the frame of the BioH_2Power project, is the identification of a system for both desulphurization and dehalogenation of landfill biogas. Such system should be capable of reducing to less than 0.1 ppm the substances present in the biogas that are undesirable for both reforming and Molten Carbonate Fuel Cell (MCFCs) catalysts. A commercial adsorbent material was tested for desulphurization of the biogas extracted from the Montescarpino MSW landfill in Genoa, Italy, managed by Asja Ambiente Italia S.p.A. Moreover, two commercial activated carbons (Norit R1540W and RB4W) were tested for the removal of nine halogenated hydrocarbons in a model biogas, at the laboratories of Politecnico di Torino. Results from hydrogen sulphide (H_2S) removal revealed a difference of 66% between the total adsorptive capacity reported by the manufacturer and the value obtained by means of our desulphurization tests. This difference is most likely due to the presence of many other hydrocarbons in the landfill biogas that are also adsorbed on the activate carbon, reducing significantly its selectivity and sulphur compounds uptake capacity [1,2]. As far as the dehalogenation of the model biogas is concerned, the obtained results show that both commercial activated carbons could remove the majority of the chlorinated species but with different breakthrough times, as it can be seen in figure 1 for the Norit RB4W activated carbon. The uptake capacity for the chloromethane and chloroethane species is negligible. On the other hand, 1,1,2,2-tetrachloroethane has the highest uptake capacity (6.79 and 7.76 wt%, for R1540W and RB4W, respectively). The adsorption trend may be explained as a function of more than one parameter. The adsorption capacity increases with the increasing molecular weight of the considered species, although this trend is not absolute. A different charge distribution (polarization effect) on the molecules due to the different numbers of chlorines and their positions should also be considered to better correlate the adsorption trend. Moreover, the degree of unsaturation should also be taken into account. Even though for most of the studied chlorinated molecules, adsorption capacity increases with molecular weight; 1,1,1-trichloroethane, trichloroethene, 1,3-dichloro 1-propene (cis) and 1,3-dichloro 1-propene (trans) do not follow this trend. Hence, the adsorption capacity of these compounds can be explained as a function of symmetry as well. In this way, it was verified that tested activated carbons are not able to completely remove all the undesirable sulphurated or halogenated compounds present in the landfill biogas. Therefore, on the basis of our results, a cost-estimation was made for the comparison of an adsorption system and a scrubbing method for biogas purification. High operation costs for the use of activated carbons suggest that gas-scrubbing is the lowest cost solution. However, in order to reach the high standard values required for the application of biogas in a Fuel Cell System, a combined system, scrubber + activated carbon, should be the most cost-effective technology.

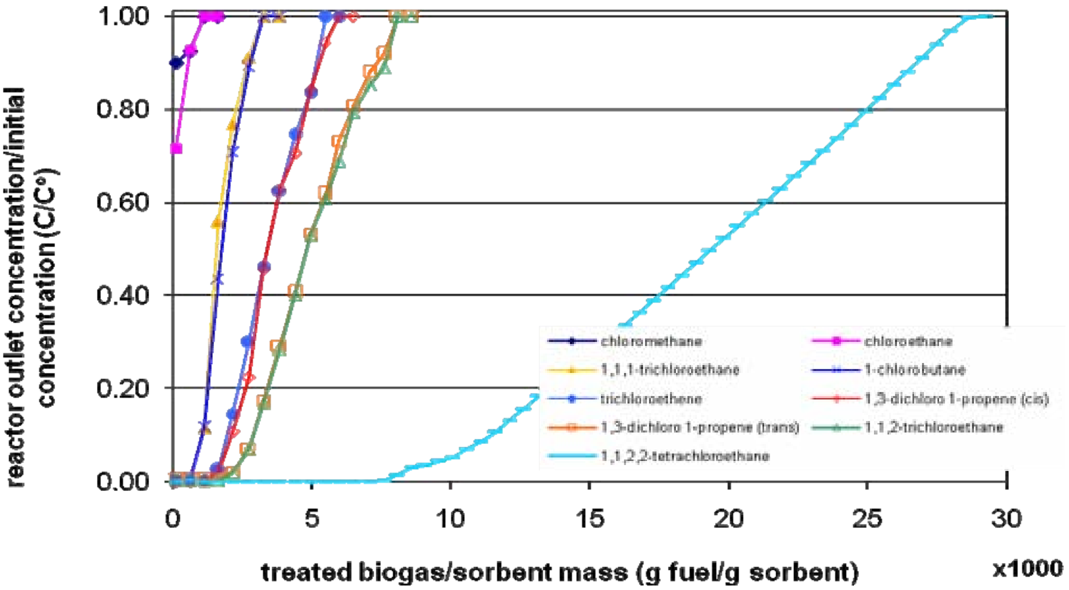


Figure 1. Adsorption uptake capacity of commercial Norit RB4W activated carbon.

References

[1]. Gordon Israelson P.E. Water Vapor Effects on Fuel Cell Desulfurizer Performance – A Decade of Field Experience. Proceedings of FuelCell2008, June 16-18, **(2008)** Denver, Colorado, USA.

[2]. Esteves I.A.A.C., Lopes M.S.S., Nunes P.M.C., Mota J.P.B. “Adsorption of natural gas and biogas components on activated carbon” Separation and Purification Technology 62 **(2008)** 281–296.

Acknowledgements

The financial support of Regione Piemonte for the BioH$_2$Power Project is gratefully acknowledged.

MODELING AND SIMULATION OF HYDROGEN REACTOR

Kolesnikov A.[1], **Mutshena M.**[1,2]

[1]*Tshwane University of Technology, Pretoria, South Africa, kolesnikova@tut.ac.za*
[2]*PBMR, Pretoria, South Africa*

Development of transport vehicles based on hydrogen as an alternative fuel requires new technical solutions for hydrogen storage and release. One of the promising technologies is application of storage tanks with AB5 metal hydrides in form of finely dispersed powder (particle size below 5 μm) [1]. By controlling the pressure and temperature distributions inside the bulk powder material, it is possible to influence the physical and chemical kinetics on the surface and in the body of metal hydride particles. The required rate of hydrogen reaction, therefore, can be maintained [2].

To design and operate a hydrogen reactor, an accurate mathematical model is required.

In this paper a mathematical model for 3-D transient analysis of heat and mass transfer in a new AB5 hydride-based hydrogen reactor was developed and simulation results for a section of the axisymmetrical reactor have been presented.

The model consists of mass and energy conservation equations for metal hydride bed and reactor's body, including newly designed heat sinks immersed in the bed.

The COMSOL software was used to solve the system of transient 3D PDEs.

The physico-chemical characteristics of the new metal hydride (including equilibrium gas pressure curves) were evaluated in the HySA laboratory of South African Institute of Advanced Materials Chemistry [3].

The model was initially validated against the data published in the reference [4].

The developed model was used to evaluate the dynamics of hydrogen release in a storage tank for supplying the 500 W fuel cell installed on the bicycle under typical South African weather conditions. The simulation results are presented as spatio-temporal distributions of temperature, pressure, and hydride density together with integral hydrogen release curve. The sensitivity of results to the model parameters has been discussed.

References

[1]. B. Sakintunaa, F. Lamari-Darkrimb, M. Hirscherc, "Metal hydride materials for solid hydrogen storage:A review", International Journal of Hydrogen Energy (**2007**), 32, 1121–1140.

[2]. S. Srivastava, O.N. Srivastava, "Hydrogenation behaviour with regard to storage capacity, kinetics, stability and thermodynamic behaviour of hydrogen storage composite alloys, LaNi5/La2Ni7, LaNi3", Journal of Alloys and Compounds, (**1999**), 290, 250–256.

[3]. M.V.Lototsky, R.V.Denys, V.A.Yartys "Combustion-type hydrogenation of nanostructured Mg-based composites", In. Symp. On Metal-Hydride Systems (MH-2008) **2008**, Reykjavik,

[4]. A. Freni, F. Cipitì "3D Dynamic Simulation of a Metal Hydride-Based Hydrogen Storage Tank" , Proceedings of the COMSOL Conference **2008** Hannover, 1-7.

OP-III-B-5

PARTIAL DEHYDROGENATION OF KEROSENE AS HYDROGEN SOURCE FOR FUEL CELLS IN MICROSTRUCTURED REACTORS

Kolb G., **Tiemann D.**, **Hessel V.**

Institut für Mikrotechnik Mainz GmbH (IMM), Carl-Zeiss-Str.18-20 D-55129 Mainz;
Tel.: ++49-6131-990-341; Fax.:-305; e-mail: kolb@imm-mainz.de

Introduction

Microstructured reactors offer benefits concerning efficiency and size reduction owing to their potential of heat integration and improved heat and mass transfer. Fuel cells are regarded as a viable energy source for mobile applications, among them for aviation purposes. However, different concepts do exist for the hydrogen supply source for fuel cells in the field of aviation, e.g. liquid and compressed storage and fuel processing of kerosene. While fuel processing of hydrocarbon fuels requires not only a reformer but also CO clean-up reactors of a complexity which is closely related to the fuel cell type supplied by the reformer [1], partial dehydrogenation of the kerosene (here expressed as a $C_{12}H_{23}$-hydrocarbon):

$$C_{12}H_{23} \rightarrow C_{12}H_{21} + H_2 \qquad (1)$$

which is readily available on board of every aircraft and represents an alternative processing route with the potential to achieve reduced system complexity, provided the dehydrogenation reaction does not change the combustion characteristics of the fuel considerably.

Catalyst Screening

Sulphur free kerosene (S content 1 ppm) was chosen as fuel for the screening tests A number of platinum based bi-metallic catalysts were investigated, the second metal being one of the elements tin, gallium, iridium, rhenium, sodium, potassium and others. All catalysts were wash-coated onto aluminium foams and tested at temperatures between 300°C and 400°C at pressures between 5 and 15 bar.

Most of the catalysts showed rapid deactivation during the first few hours of testing despite the absence of sulphur in the feed. However, a platinum based formulation could be identified, which showed stable performance at 15% conversion according to equation (1), a VHSV of 1400 L/(h g_{cat}) for 100 hours as a result of the optimization work.

Demonstrator

The medium-term stable catalyst formulation described above was then incorporated into a modular demonstrator (see Fig.1). The energy required to drive the endothermic dehydrogenation reaction was foreseen to originate from the combustion of fuel cell anode off-gas and kerosene in a future technical process. Thus the modules of the demonstrator had a plate heat-exchanger design composed of layers for energy supply carrying micro-structured heating channels, which were fed with hot gas and reaction layers and carried catalyst coated onto aluminium foam modules.

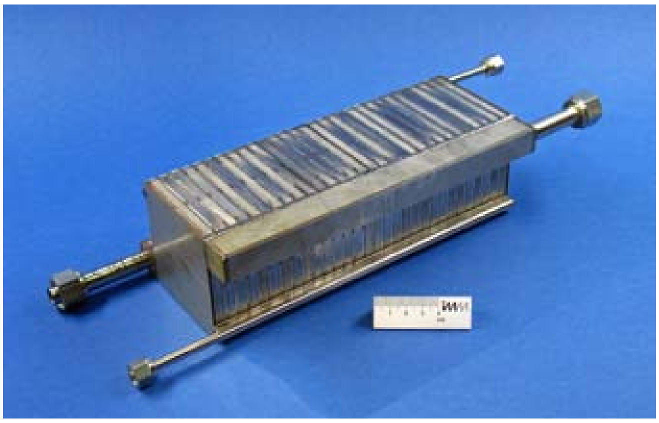


Fig. 1 Hot gas driven de-hydrogenation reactor

Up to 18 L/h kerosene were fed into the reactor and the maximum flow rate of hydrogen produced exceeded 100 L/h. It is to the authors' knowledge the first prototype partial dehydrogenation reactor for fuel cell applications of that size presented in open literature.

Besides the hydrogen product, light hydrocarbons such as ethylene and propylene were detected in the gaseous product, in concentrations between a few hundred ppm and 2 Vol.% depending on the reaction conditions. Such by-products would require additional purification steps because they would poison at least PEM fuel cell anodes.

Acknowledgement

The work presented here was funded by Airbus Deutschland GmbH and the German Ministry of Economics and Technology in the scope of the project ELFA-BREZEN as part of the national aerospace research program.

References

[1] Kolb, G.; *Fuel Processing for Fuel Cells,* 1 Ed.; Wiley-VCH, Weinheim (2008).

TESTING MEMBRANE REACTORS AT SCALE: WGS-EXPERIMENTS WITH THREE Pd MEMBRANE TUBES OF 50 cm LONG

Hui Li, J. Boon, J.W. Dijkstra, J.A.Z. Pieterse

Hydrogen & Clean Fossil Fuels, Energy research Centre of the Netherlands,
P.O. Box 1, NL1755ZG Petten, The Netherlands, li@ecn.nl

One attractive approach for CO_2 capture in power plants is to carry out the water-gas shift (WGS) reaction in a Pd-based membrane reactor, where the chemical reaction and H_2/CO_2 product separation occur at the same time. The reactions can be carried out more efficiently as the equilibrium will be shifted due to the selective removal of H_2. When integrated in a natural gas fired power plant, these reactors allow for power production from the hydrogen stream while simultaneously CO_2 is captured in the retentate side and available for underground storage. Recently, ECN has constructed a process development unit (PDU) for testing membrane reactors. It has a capacity of 8 tubular membranes of 50 cm long and can be operated up to 40 bara and 600°C. The PDU will demonstrate the feasibility of membrane reactors at a bench scale size, and at the conditions that are present in power plants with pre-combustion CO_2 capture using hydrogen membranes. It is used for testing of reactor concepts, and the study of membrane and catalyst characteristics.

The present contribution describes membrane-enhanced water-gas shift reaction with three parallel highly perm-selective Pd composite membranes in the PDU with a length of 50 cm (44 cm effective) and with a palladium layer of *ca.* 5.6 μm, reaching a total membrane surface area of 580 cm^2 configuration. Working conditions were: 400°C and 20-35 bar(a) feed pressure, composition: 4.01% CO, 19.24% CO_2, 15.43% H_2O, 1.20% CH_4 and 60.12% H_2. Commercial noble metal water-gas shift catalyst was inserted at the feed side of the reactor tubes. Feed flow rate of 30-90 Nl/min were used and a N_2 counter-current sweep at 15 bar was applied.

The pure H_2 permeance of the three membranes was measured as $2.7 \cdot 10^{-6}$ mol/m^2.s.Pa at 400°C with a feed/permeate pressure of 2.1/1.1 bar(a) under no-sweep conditions and remained stable for 27 days during the WGS-reaction test while the pure N_2 permeance of three membranes was $2.6 \cdot 10^{-9}$ mol/m^2.s.Pa at 400°C. CO conversion was observed to be far beyond the equilibrium conversion at 400°C, increased with feed pressure and decreased with feed flow rate (see Figure 1). CO conversion and H_2 recovery amounted up to 92% at a feed/sweep flow rate of

30/19.6 Nl/min (space velocity of *ca.* 3000 $Nm^3m^{-3}h^{-1}$) and feed/permeate pressure of 35/15 bar(a). Higher conversion and H_2 recovery over 95 % are within reach by lowering the permeate pressure. Stability tests showed that CO conversion remained stable under different feed pressures and under reduced steam content in the feed, indicating that membrane degradation due to carbon formation was not observed, also not under low steam conditions resulting in a high carbon formation tendency.

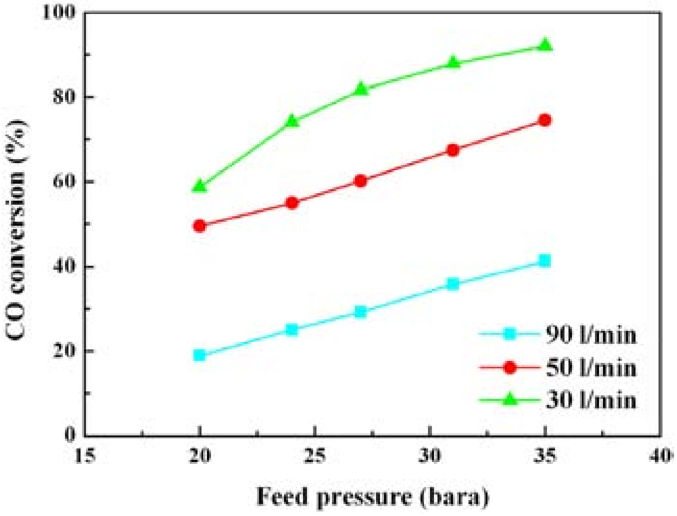


Figure 1: CO conversion as function of the feed pressure and flow rate.

The results of the experiments are analysed with a 1-dimensional axial balance model accounting for reaction, membrane permeation and heat effects. This allows for estimation of the membrane permeance under WGS conditions. The results are compared to pure H_2 permeance measurements and to similar analysis of measurements using a H_2/N_2 mixture, which allow for assessment of the relative contribution of mass transfer.

NOVEL APPROACH FOR MUNICIPAL SOLID WASTE BIOGAS REFORMING INTO HYDROGEN FOR FUEL CELL POWERED GENERATORS

Lysikov A.I.[1], Okunev A.G.[1], Molodtsov D.V.[2], Maslikov V.I.[2]

[1]Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia, lyanig@catalysis.ru
[2]Saint-Petersburg State Polytechnical University, St. Petersburg, Russia

Among the different municipal solid waste (MSW) impacts, biogas emission is the one with the highest environmental impact because of its greenhouses effect. Single MSW dump emits up to several thousands of cubic meters per hour of biogas which consists of 45-65 % of methane. Biomethane utilisation in increasingly popular nowadays on-site landfill gas insinerators results in a flue gases contaminated with toxic and greenhouse pollutants, including carbon dioxide (30-40 vol.%), hydrogen disulfide (200 ppm) and others [1].

Our study focuses on the development of the alternative environment friendly treatment sequence that is suitable for electricty production from biogas. The sequnce comprises CO_2 and H_2S separation, biogas conversion to CO free hydrogen rich gas, hydrogen oxidation in polymer-electrolyte fuel cell.

This paper deals with the experimental study of the second step in the sequence, i.e. purified biogas reforming into CO free hydrogen rich gas. The sorption-enhanced biogas reforming scheme [2] was adopted for hydrogen production. The scheme comprises one pot catalytic steam reforming of methane coupled with high temperature CO_2 absorption using CaO sorbent. A pilot scale reformer was designed (fig.1) which has up to 43 liter H_2/hour output and use temperature swing sorbent regeneration method. The reactors were loaded with the mix of porous calcium oxide granules, prepared in the Boreskov Institute of Catalysis [3], and commercial Ni catalysts NIAP-03 (11 wt.% NiO). The methanator was loaded with commercial catalyst NIAP-07 (36 wt.% NiO).

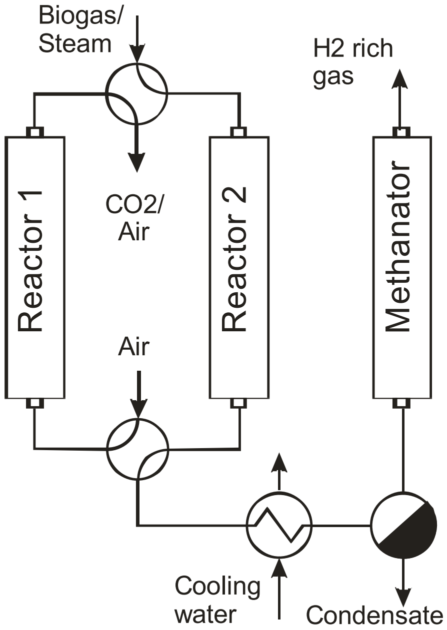


Fig. 1. Biogas reforming scheme.

Biogas was modelled using three different compositions of the methane, CO_2 and nitrogen mixed in the ratios: 94,8; 5,2; 0 об.% (mixture I), 35,4; 54,9; 9,7 об.% (mixture II) and 44,6; 40; 15,4 об.% (mixture III). The reactors were temperature swung between 680 °C (reforming step) and 820 °C (regeneration step). The methanator temperature was set to 400 °C. The reforming pressure was 1,6 atm, H_2O/C ratio was 4. During regeneration step the reactors were purged with 140 L/h flow of air. The experimental data on biogas reforming are listed in the Table 1.

Table 1

Sorption enhanced biogas steam reforming data.

Mixture N	Biogas flow, l/h	Reformate flow l/h,	The reformate composition, vol.%					
			H_2	CH_4	CO	CO_2	H_2O	N_2
I	10,9	42,6	98,0	1,0	<0,003	<0,01	0,98	0
I	6,52	25,7	97,3	1,7	<0,003	<0,02	0,98	0
I	3,74	13,2	98,0	1,0	<0,003	<0,01	0,95	0
II*	10,9	16,8	94,8	0,8	<0,003	<0,04	1,09	3,3
II	10,9	16,8	95,3	0,2	<0,003	<0,04	1,16	3,3
III	10,98	20,4	93,3	0,5	<0,003	<0,03	1,11	5,3
III	6,58	12,9	93,5	0,3	<0,003	<0,03	1,08	5,1
III	3,78	6,9	93,5	0,3	<0,003	<0,02	1,05	5,1

* - Methanator temperature is 300 °C.

The methane was the main impurity in the product hygrogen rich gas. The residual methane content decreases with decrease in CH_4 content in biogas from 1-2 vol. % for mixture to 0.3-0.5 vol.% for mixture III. The CO level in all runs was below detectable limit of 3 ppm, that is acceptable for use in solid polymer electrolyte fuel cells.

It is concluded that the soprtion enhanced reforming is a simple and reliable approach that can be used in suggested biogas to electricity conversion sequence.

References

[1]. M. P. Fedorov, V. V. Korablev, V. I. Maslikov and E. O. Ioksha, *Ecology and life*, **2008**, 4, 16-22.

[2]. A. I. Lysikov, S. N. Trukhan and A. G. Okunev, *International Journal of Hydrogen Energy*, **2008**, 33, 3061-3066.

[3]. A. I. Lysikov, A. N. Salanov and A. G. Okunev, *Industrial & Engineering Chemistry Research*, **2007**, 46, 4633 - 4638.

TWO STEP PROCESS OF OBTAINING LOW BENZENE CONTAINING FUELS FROM ETHANOL

Makarfi Y.I.[1], **Tretyakov V.F.**[1,2], **Frantsuzova N.A.**[1], **Tretyakov K.V.**[2]

[1]*Lomonosov Moscow State Academy of Fine Chemical Technology,*
119571 Moscow, Russia
[2]*A.V. Topchiev Institute of Petrochemical Synthesis, Moscow, Russia*
yusufisa@yahoo.com

Recent reports have shown that a lot of progress is being made in utilizing ethanol obtained from biomass as a fuel in internal combustion engines. However, this advancement is dampened by the need to redesign engines that will easily utilize ethanol without having to blend it. Among the advantages of ethanol over fossil fuel is the reduction in net emission of carbon dioxide. At the same time among its shortcomings is the fact that crude oil does not only supply fuels but also a wide range of hydrocarbons through primary and secondary treatment of the raw crude.

A more convenient way of fully substituting crude oil with ethanol should ensure that products obtainable from crude oil can be produced from ethanol. To this effect, much work has been done in converting the liquid obtained from biomass into a wide range of hydrocarbons. As reported in [1], based on reaction conditions, various hydrocarbons can be obtained by passing ethanol over modified zeolite catalysts. However, It has been observed that the concentration of certain aromatic compounds in the conversion product is relatively high compared to modern day acceptable standards in transport fuels (less than 1%). Taking this into consideration, We have developed an effective way of hydrogenating the liquid obtained from ethanol conversion using nano-structured Pt-Rd catalyst. The concentration of aromatic hydrocarbons in the upgraded liquid reduces by 50%, with practically no benzene. (Table1.) This makes it possible to produce transport fuels with aromatic content 12-35 %mass. (diagram1). The research shows that ethanol is capable of substituting crude oil not only as a source of transport fuel, but as a raw material for other petrochemicals.

Table 1. Material balance for 1 tonne of liquid obtained from ethanol conversion.

Compound	Input		Output	
	т	% mass	т	% mass
C_1-C_4	0.09	7.20	0.10	8.13
C_{5-9}	0.20	16.00	0.88	70.79
Benzene	0.02	1.60	0.00	0.01
Toluene	0.18	14.40	0.00	0.00
Ethylbenzene	0.04	3.20	0.00	0.36
m,p, Xylenes	0.25	20.00	0.01	0.63
Orto xylenes	0.14	11.20	0.03	2.44
Ethylmethyl benzene	0.08	6.40	0.08	6.15
Other aromatic hydrocarbons	0.00	0.00	0.11	9.05
Hydrogen	0.25	20.00	~	~
Coke +loss	-	-	0.03	2.44
Total	1.25	100	1.25	100

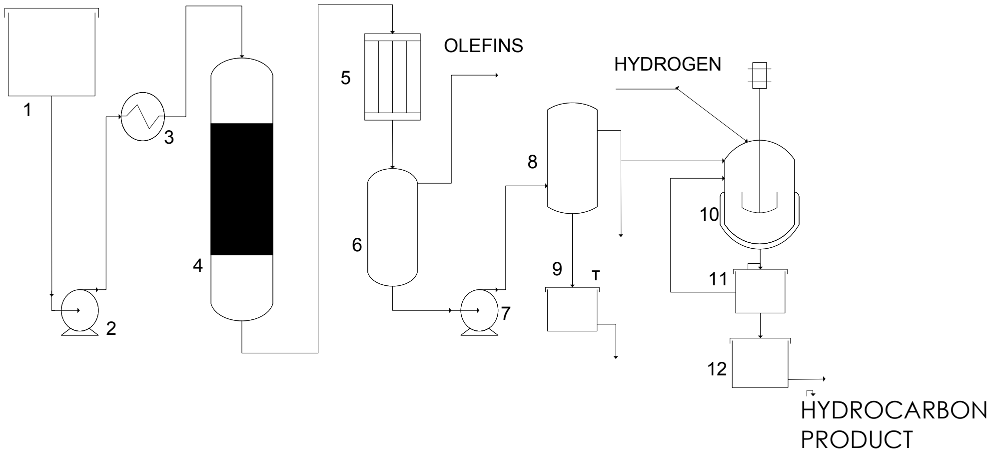


Diagram 1. SETUP FOR OBTAINING TRANSPORT FUELS FROM ETHANOL

1 – Bio-ethanol tank, 2 - Pump 3 – Heat exchanger, 4 – Conversion reactor, 5 - Condenser, 6 -separator, 7-Pump, 8-Separator, 9-Water tank, 10 – Hydrogenation reactor, 11 – Filter, 12-product tank.

References

[1]. Y.I.Makarfi et al. Conversion of Bio-ethanol over zeolites; Chemical Engineering Journal; 2009; V.154 №-3 – pp 396-400

DEVELOPMENT OF CATALYTIC REACTOR FOR COMBUSTION OF NATURAL GAS FOR ENVIRONMENTALLY FRIENDLY GAS TURBINE POWER PLANTS

**Ismagilov Z.R.[1], Kerzhentsev M.A.[1], Shikina N.V.[1], Yashnik S.A.[1],
Zagoruiko A.N.[1], Khairulin S.R.[1], Parmon V.N.[1],
Zakharov V.M.[2], Braynin B.I.[2], Favorski O.N.[2]**

[1]Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia, zri@catalysis.ru
[2]Central Institute of Aviation Motors, Moscow, Russia

In the last decades, catalytic combustion has received an increasing interest as an ultra-low emission technology for gas turbines, providing possibility to decrease toxic emissions of HC, CO, NO_x [1-3]. In 2001, Catalytica Energy Systems Inc. (USA) jointly with Kawasaki Heavy Industries (Japan) launched commercial production of small Kawasaki 1.4 MW turbines supplied with a catalytic combustion reactor, providing a decrease of NO_x emissions below 3 ppm.

At present, catalysts for gas turbines are manufactured mainly as monoliths prepared from metal foil with deposited porous washcoat and catalytically active component (usually Pd). In this work, we present results on development and study of catalytic combustion reactor alternative design for methane catalytic combustion in mini gas turbines of 400-500 kW power with regenerative cycle, intended for decentralized power supply. The small power of these turbines results in reduced catalyst loading reactor and makes possible the use of granular catalysts which are more suitable for this application and can be easily manufactured.

For successful accomplishment of design of this type of batch reactor we had to explore several problems such as 1) high activity of catalysts at low temperatures and its high temperature stability, 2) selection of shape and size of granules, 3) reactor design with low pressure drop, 4) optimization of combined catalyst loading in the reactor.

In this paper, we present results on modeling and experimental study of three types of structured loadings of the reactor: variation of catalytic activity and shape of granules for uniform loading and combined loading consisting of two or three different catalyst beds [4]. In a combined loading the first bed is formed of ring-shaped highly active Pd-ceria catalysts initiating methane combustion at low temperature, the second bed, where the main part of methane is burned, is formed of ring-shaped thermally stable Mn-La oxide catalyst, and the third (optional) bed is made of spherical granules of Pd containing catalyst used for afterburning of trace amounts of methane and CO.

Based on the results of the calculations, optimum conditions for methane combustion in the catalytic combustor providing high degree of methane conversion were determined: the use of the combined catalyst package containing 10-20% of highly active Pd-Ce catalyst and 90-80% of thermally stable Mn-La catalyst in the form of rings of 7 mm diameter and 7 mm height with a 3 mm orifice; methane concentration 1.5% and the inlet temperature of methane-air mixture 450-550°C.

Pilot study of methane catalytic combustion was performed in a stainless-steel tubular vertical reactor with an inner diameter of 76 mm and a catalyst loading 1,3 dm^3, equipped with thermocouples and sampling probes permitting the study of profiles of temperature and concentrations of along the catalysts bed. The results of the tests proved to be in good agreement with the results of the modeling. The experiments with the catalyst package containing Pd-Ce catalyst (15%) in combination with Mn-La catalyst (85%) at CH_4 concentration 1.5% and variation of the inlet temperature from 480 to 600°C showed high degree of methane combustion. The level of emissions was as low as: NOx < 1 ppm, CO < 3 ppm, HC < 10 ppm.

Fig. 1. Prototype combustor.

Based on the results of these studies, a prototype catalytic reactor for a gas turbine with a power 380 kW was designed and fabricated (Fig. 1). The combustor has a preheating chamber to heat the catalyst to ignition temperature by hot combustion gases and an annular catalyst module with a catalyst loading of 70 kg.

Testing of the prototype combustor demonstrated high efficiency of methane combustion (>99.97%) and low emission: NOx < 1 ppm, CO < 10 ppm, HC < 10 ppm under the following conditions: inlet temperature 560°C, outlet temperature 900°C, GHSV = 31200 h^{-1}, 5 atm.

References

[1] W.C. Pfefferle, J. Energy, 2 (1978) 142.
[2] R. Carroni, V. Schimdt, T. Griffin, Catalysis Today, 75 (2002) 287.
[3] S. Cocchi, G. Nutini, M.J. Spencer, S.G. Nickolas, Catalysis Today, 117 (2006) 419.
[4] Z.R. Ismagilov, N.V. Shikina, S.A. Yashnik et al. RF Patent No 2372556.

Acknowledgements

This work was supported by Prezidium of RAS Project # 19.4.

OP-III-B-10

CATALYTIC OXIDATION OF LEAN BIOGAS-AIR

Shahamiri S.A., Wierzba I.

Department of Mechanical and Manufacturing Engineering, Schulich School of Engineering, University of Calgary, Alberta, Canada, iwierzba@ucalgary.ca

Low heating value gaseous fuel mixtures, such as those derived from the processing of biosources and landfill gases have a common feature of being made up of primarily methane with relatively large concentrations of the diluents carbon dioxide with some nitrogen. However, it is widely known that the presence of such diluents with the methane will seriously impede its oxidation mainly due to the low fuel concentration and the very low associated resulting temperatures [1,2]. The successful combustion of these gases needed to permit their effective exploitation in common combustion devices and processes requires further research and development. The catalytic oxidation of homogeneous fuel-air mixtures containing low concentrations of fuel may represent a potentially effective approach for their efficient and clean combustion [3,4,5]. In the present work the catalytic oxidation of lean homogeneous mixtures of CH_4-CO_2 and air in a Pt/Al_2O_3 packed bed reactor was modeled using detailed surface and gas reaction chemical kinetics. The model is based on two-phase treatment approach and accounts for the effects of the transport processes between the two phases on the reaction rates. It was applied to simulate a non-adiabatic lab scale reactor fed with preheated homogeneously premixed fuel and air and operating at atmospheric pressure [6]. The results were obtained for inlet feed temperatures of 600 - 900 K and equivalence ratios of 0.15 - 0.55 with concentration of CO_2 in the fuel ranging from 0 to 90%. It was shown that for these equivalence ratio values the presence of CO_2 did not hinder the oxidation rates markedly until the fuel contained more than ~70% of carbon dioxide, when the oxidation rate became affected significantly. As it can be seen (Fig 1) this is especially pronounced with the higher equivalence ratio feed. Moreover, the effects of using higher values of equivalence ratio had a greater positive effect on the oxidation of methane than its impeding by equivalent increases in the concentration of CO_2 in the fuel. It is also shown that for an equivalence ratio of 0.15, the energy released by the reaction appears insufficient to provide the preheating required over the feed mixture temperatures considered (Fig 2). For the feed equivalence ratio of 0.35 the heat released is greater than required for preheating when T_{inlet} > ~700 K and concentration of CO_2 in the fuel is less that 60%. For the higher 0.55 equivalence ratio case the positive heat balance is observed for almost all the cases considered.

On this basis it can be seen that care is needed to insure that although the catalytic reactor may convert the very low concentrations of methane present, the associated energy release must be in excess of that needed for preheating the feed.

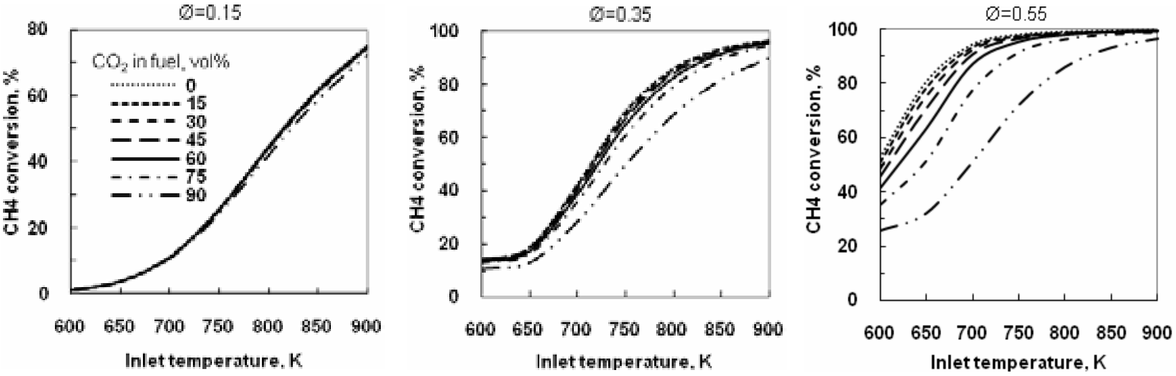


Fig. 1. Effect of inlet temperature on CH_4 conversion in presence of CO_2; same legends.

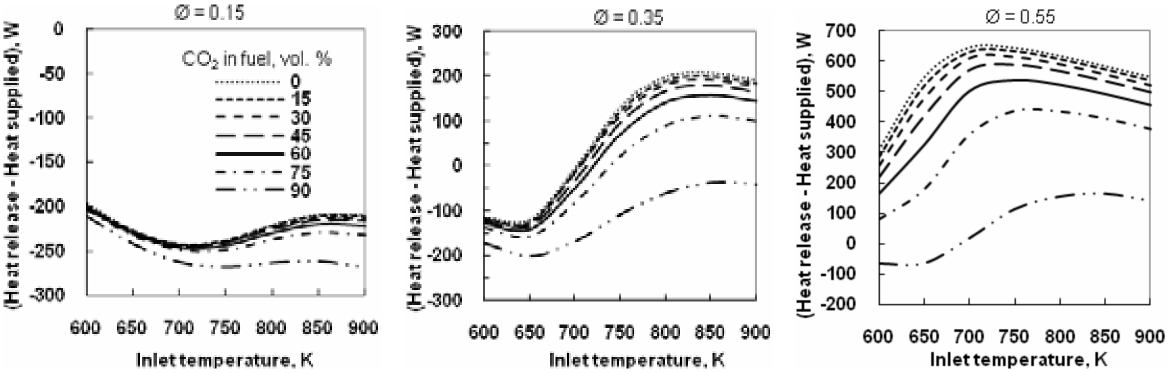


Fig. 2. Heat gain as a function of feed inlet temperature; same legends.

References

[1]. Y. Lafay, B. Taupin, G. Martins, G. Cabot, B. Renou and A Boukhalfa, “Experimental study of biogas combustion using a gas turbine configuration”, Exp. Fluids, **2007,** 43 395-410.

[2]. F.Liu, H. Guo and G.J. Smallwood, “The chemical effect of CO_2 replacement of N_2 in air on the burning velocity of CH_4 and H_2 premixed flames”, Combust. Flame, **2003,** 133 495-497.

[3]. S. Eriksson, M. Boutonnet and S. Jaras, ”Catalytic combustion of methane in steam and carbon dioxide-diluted reaction mixtures”, Appl. Catal., A, 2**006,** 312 95-101.

[4]. J.J. Witton, E. Noordally and J.M. Przybylski,” Clean catalytic combustion of low heat value fuels from gasification processes”, Chem. Eng. J., **2003,** 91 115–121.

[5]. Y. Chao, G. Chen, H. Hsu and J. Hsu,” Catalytic combustion of gasified biomass in a platinum monolith honeycomb reactor”, Appl. Catal., A, **2004,** 261 99-107.

[6]. S.A. Shahamiri and I. Wierzba, “Simulation of catalytic oxidation of lean hydrogen–methane mixtures”, Int. J. Hydrogen Energy, **2009,** 34(14) 5785-5794.

Acknowledgements

The financial supports of Natural Sciences and Engineering Research Council of Canada (NSERC), Centre for Environmental Engineering Research and Education at the University of Calgary (CEERE), Canadian Prairie Air & Waste Management and Northern Section (CPANS), ConocoPhillips Canada and Talisman Energy Inc are greatly appreciated.

OP-III-B-11

STATE-OF-THE ART REACTOR DESIGN FOR HIGH-CAPACITY OIL-REFINING PROCESS

Kapustin V.M.

OAO VNIPIneft;
Gubkin Russian State Oil & Gas University, Moscow, Russia
E-mail: vkapustin@vnipineft.ru

At present, special attention is given to an oil conversion degree. Increasing the oil conversion depth and upgrading heavy ends are achieved due to presence of destructive processes in process flow diagrams of refineries. Destructive processes are presented by various chemical reactions: cracking, hydrogenolysis, hydrogenation-dehydrogenation, dehydrocyclization, alkylation, isomerization, polycondensation, etc. These processes run in special-purpose vessels, so-called reactors. A reactor design depends on peculiarities of a particular reaction and process conditions (temperature, pressure, catalysts available, etc.).

Permanent improvement of technologies and development of new efficient catalysts contributes to modernization and creation of new reactor equipment. In turn, emerging new structural materials offers the opportunity for changing the conditions of chemical reaction, using next-generation catalytic systems and necessitates developing and creating of new reaction facilities.

Of particular interest is the evolution of a catalytic cracking reactor-regenerator block, having been updated concurrently with development of catalytic systems, from a moving-bed reactor to a riser A trend to involve heavy petroleum feedstock and resides in processing necessitates modernizing a regeneration unit with a special heat-rejection device, developing special feeding equipment for reactors and creating a fundamentally new ultra-short contact time reactor (millisecond reactor).

A number of new design solutions have been used for the reactor of a new VGO catalytic cracking complex of OAO TAIF-NK in Nizhnekamsk built on the basis of a domestic technology developed by INKhS RAN, OAO VNII NP and OAO VNIPIneft. These R&D allowed achieving global competitive performance.

Ever-heavier feedstock used in hydrocracking necessitates running processes in a moving catalyst bed, which, in its turn, results in more and more complicated reactor design (H-Oil and LC-fining).

Similar trends caused by a necessity of using a moving and permanently regenerating catalyst are observed in catalytic reforming and solid-acid alkylation processes (UOP).

Thus, the reactor design is now permanently renewed and upgraded, a share of nonstandard reactor equipment is enhanced which permits to involve in processing increasingly heavier feedstock and evidences of the emergence of a new phase of developing thermal destructive and catalytic processes in oil refining and petrochemical industry.

HYDRODESULFURIZATION OF 4,6-DIMETHYLDIBENZOTHIOPHENE ON NiMoP/Al_2O_3 CATALYST IN A TRICKLE BED MICROREACTOR

García-Martínez J.C., Lobo R., Pérez Cisneros E.,
Ochoa Tapia J.A. and De los Reyes J.A.

Universidad Autónoma Metropolitana-Iztapalapa, Área de Ingeniería Química
Av. Rafael Atlixco 186, Iztapalapa, 09340 México, D.F.
jarh@xanum.uam.mx

In order to reach current enviromental requirements regarding the content of sulfur in diesel, it is essential to consider the existence of sulfur-containing molecules of low reactivity (i.e. dialkildibenzothiophenes like 4,6-dimetildibenzothiophene,4,6-DMDBT) in the hydrodesulfurization (HDS) process. In these reactions, sulfur-containing molecules react with hydrogen in presence of a catalyst (usually a sulfided CoMo or NiMo supported on alumina) at temperatures between 573-623 K and hydrogen pressure 5.1-101.0 MPa [1] in a trickle bed reactor. In recent time, reactive distillation (RD) has been considered to be a highly promising process because it combines the requirements of in situ separation with reaction and the temperature and pressure are lower than those of the conventional processes. Some of us have reported interesting simulation results based on this technology [2]. For these conditions it is needed to screen catalysts at the RD operation conditions in a three phases-system, analogous to a trickle bed reactor, where transport phenomena and hydrogen solubility have not been fully understood. Besides, experimental devices must consider low operating and construction costs along with low emissions. Thus, some authors reported results on HDS using trickle bed microreactors [3]. However, none of them have studied a range of operation conditions such as those required for RD. Moreover, the choice of appropriate solvent and model molecules are relevant to obtain information useful for industrial purposes.

The aim of this paper was to carry out experimental work in a down-flow trickle bed microreactor under RD conditions. This reactor (diameter of 4 mm and a length of 30 mm) was packed with a commercial sulfided catalyst (NiMoP/Al_2O_3) diluted with inert SiC for the HDS of 4,6-DMDBT. The influences of experimental conditions like low pressure and temperature and a modification of solvent were evaluated in the interphases mass transfer processes and the hydrogen solubility in the liquid phase.

Previously, it was possible to define experimental conditions such as gas and liquid flow rates leading to small deviations to plug flow, trickle flow, high holdup and low pressure drop. Fig. 1 shows experimental data for rate of reaction for HDS of 4,6-DMDBT with decaline and dodecane as solvents.

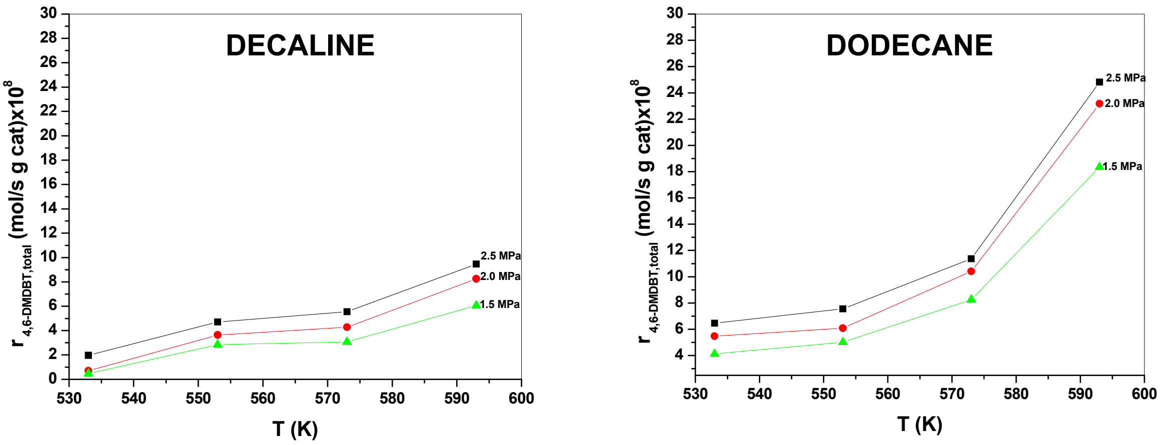


Figure 1.- 4,6-DMDBT reaction rates at different temperatures and pressures for two solvents.

One can note that reaction rate followed different trends for the two solvents when increasing temperature. An analysis in terms of mass transfer coefficients (see equation A) for hydrogen revealed that gas to liquid transfer may be controlling for the experiments where decaline was used as solvent. For both solvents, thermodynamic calculations for hydrogen solubility under the studied pressure and temperature pointed out that enough hydrogen would be available to react with 4,6 DMDBT. Mass transfer coefficients (gas to liquid, liquid to solid) calculations will be presented and further discussion will be provided.

$$\frac{d^2 x_{H_2,L}}{dz^{*2}} - Pe\frac{dx_{H_2,L}}{dz^*} - \beta = \zeta$$ [A] where

$$\beta = \left\{\left(K_L a_G\right)_{H_2} + k_H^0\right\}\frac{L\,Pe}{u_L}\ ,\quad \zeta = \left\{\left(K_L a_G\right)_{H_2}\left[\frac{C_{H_2,G}/H_{H_2}}{C_{H_2,L}} - 1\right] + k_H^0\right\}\frac{L\,Pe}{u_L}\ ,$$

As a conclusion, a set of experimental conditions was found for a trickle bed microreactor in order to evaluate catalysts for an alternative RD HDS process.

References

[1]. Xiaoling, M.; Kinya, S.; Isao M. Hydrodesulfurization Reactivities of Various Sulfur compounds in Diesel Fuel. *Ind. Eng. Chem. Res.,* **1994**, 33, 218.

[2]. Cárdenas-Guerra, J. C., López-Arenas, T., Lobo-Oehmichen, R. & Cisneros, E. S., *Computers & Computers & Chem. Eng.* **34** (2010) 196 and references herein.

[3]. Pitault, I., Fongarland, P., Mitrovic, M., Ronze, D. & Forissier M., *Catalysis Today, 98 (2004) 31.*

Acknowledgements

J. C. García-Martínez thanks CONACYT for the scholarship (179608).

OP-III-B-13

ADDITIVE EFFECTS OF TYRE RUBBER CONSTITUENTS UPON COAL LIQUEFACTION

Sugano M.[1], Kashiwagi O.[1], Iwabuchi Y.[1], Tsuge T.[1] and Hirano K.[1]

Nihon University, Graduate School of Science and Technology, Department of Materials and Applied Chemistry. E-mail: sugano@chem.cst.nihon-u.ac.jp

Introduction It is well known that the amount of waste tyre increases every year, and a numerous amount of waste tyre is landfilled or dumped all over the world, which causes environmental problems, such as destruction of natural places and the risk of fires. Therefore, investigating the effective method for processing of waste tyre is a serious problem. It was reported that liquefaction of tyre to obtain fuel is one of the processing method of waste tyre [1,2]. Therefore, coprocessing of waste tyre and coal as one of the effective processing method of both materials has been investigated. On coprocessing, the synergistic effects, such as the increases of conversion [3], the yields of oil [4] and asphaltene [3,5] constituents, were reported in comparison with the result of individual liquefaction of waste tyre or coal alone. In this study, coprocessing of two kinds of coal with two kinds of tyre rubber constituents is carried out to discuss the additive effect of the rubber constituent and the effect of coal rank on coprocessing.

Experimental The coal samples (Wyoming subbituminous and Huaipei bituminous coals) was pulverized to pass through a 60 mesh screen. The tyre rubber samples (natural rubber [NR] and styrene butadiene rubber [SBR]) were divided into small pieces (5×5×20 mm). Mixture of coal (2.5 g) and tyre rubber (7.5 g) was placed in a 100 cm^3 autoclave under an initial H_2 pressure of 5.9 MPa. The reactor was heated and maintained at 440°C for 1 h. After cooling, the gaseous products (gas) were collected and analyzed using GC-TCD. The products remaining in the reactor were successively extracted with acetone and n-hexane to separate into the acetone insoluble (residue), the acetone soluble but n-hexane insoluble (asphaltene), and the n-hexane soluble (oil) materials. The oil yield was calculated from the difference between the weight of the feed sample and that of the recovered constituents (gas + asphaltene + residue) on a daf basis. Individual liquefactions of tyre rubber (10 g) and coal (2.5 g) with decalin (5g) were carried out in a similar way.

Results and Discussion Estimating from the analytical data of used coals and tyre rubber materials (not shown in this abstract for lack of space), the content of

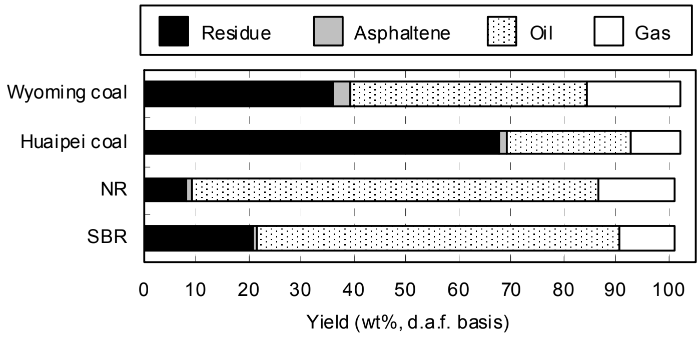


Fig. 1. Product yields after individual liquefaction of coal and tyre rubber

carbon in Wyoming coal is lower than that in Huaipei coals. The ratios of H/C in tyre rubber constituents were higher than those in coals. The product yields after individual liquefaction of coals and tyre rubber constituents are shown in Fig. 1. The exceed amounts over 100% in the product yields indicate the amount of hydrogen transferred from the pressurized H_2 gas. The yields of polar constituents (residue and asphaltene) after liquefaction of lower rank Wyoming coal were lower than those of higher rank Huaipei coal. Therefore, it was considered that the amount of polar polyaromatics in Huaipei coal was lager than that in Wyoming coal. The oil yield was high on liquefaction of tyre rubber materials. Accordingly, it was anticipated that solvent effects, such as dispersion of reactant and inhibition of partial heating in the reactor, were appeared because the oil constituent from tyre rubber formed slurry with coal particles during coprocessing. The product yields after coprocessing coal with tyre rubber materials are shown in Fig. 2. The calculated yields were obtained from the algebraic sum of the yields of individual liquefaction of tyre rubber and coal. On coprocessing coal with NR, the observed yields of polar constituents was higher than the calculated yields. Accordingly, it was considered that polymerization among the radicals from coal and NR occurred on coprocessing. In particular, the increases in yields of polar constituents by coprocessing of Wyoming coal and NR were higher than those of Huaipei coal and NR. There was little difference between the observed and calculated yields on coprocessing Wyoming coal with SBR. However, on coprocessing Huaipei coal with SBR, the yield of polar constituents decreased in comparison with the calculated yield. It was considered that radicals derived from SBR were converted preferentially into hydroaromatics through cyclization, aromatization and hydrogenation. It was expected that the increases of yields in polar constituents on coprocessing coal with SBR were inhibited since the coal radicals were stabilized by hydrogen donation and hydrogen shuttling by the hydroaromatics from SBR.

As described above, the amount of radicals from higher rank Huaipei coal was smaller than that from lower rank Wyoming coal on coal liquefaction at same temperature. Accordingly, the yields of polar constituents decreased by coprocessing

Huaipei coal with SBR because the molecular size of SBR radical was small during the stabilization with radicals from Huaipei coal. Accordingly, the solvent effects, such as hydrogen donation and hydrogen shuttling by the hydroaromatics derived from SBR, was appeared on coprocessing Huaipei coal with SBR.

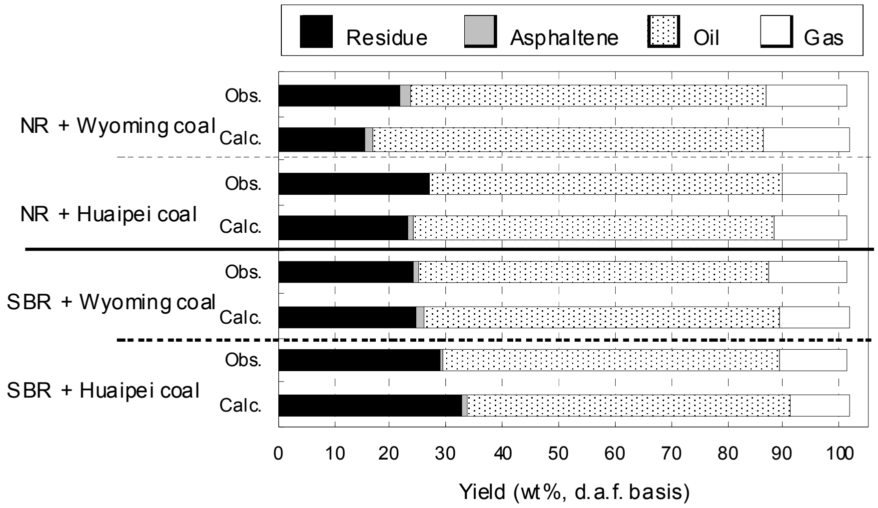


Fig. 2. Product yields after coprocessing coal with tyre rubber

Conclusions On coprocessing coal with NR, the yields of polar constituents increased in comparison with the calculated yields due to the polymerization among the radicals from coal and NR. On the other hand, polymerization was inhibited on coprocessing coal and SBR with the pressurized H_2 gas because hydrogen donation and hydrogen shuttling to coal radicals enhanced by the aromatics from SBR. In particular, the synergistic effect, such as the decrease of residue yield, appeared on coprocessing Huaipei coal with SBR. Accordingly, it was considered that the synergistic effects to upgrading on coprocessing coal with waste tyre were obtained owing to enhancement of hydrogen donation and hydrogen shuttling by the pressurized H_2 gas and aromatics derived from SBR in tyre.

References

[1]. Farcasiu, M., Smith, C. M., Prep. Papers ACS, Divi. Fuel Chem., **1992**, 37, 472-479.

[2]. Sato, Y., Kamo, T., Yamamoto, Y., Miki, K. and Kurahashi, S., Coal Science and Technology 24 (Proceedings 8th International Conference on Coal Science), **1995**, p.1539-1542.

[3]. Liu, Z., Zondlo, J.W., Dadyburjor, D.B., Energy Fuels, **1994**, 8, 607-612.

[4]. Mastral, A.M., Murillo, R., Perez-Surio, M.J., Callén, M., Energy Fuels, **1996**, 10, 941-947.

[5]. Mastral, A.M., Murillo, R., Callén, M.S., García, T., Fuel Process. Technol., **2001**, 69, 127-140.

Acknowledgements

The authors express our gratitude to Bridgestone Corporation for their providing tyre particles, natural rubber and styrene-butadiene rubber.

MODELING PRODUCT DISTRIBUTION OF PYROLYSIS GASOLINE HYDROPROCESSING ON A Pt-Pd/HZSM-5 CATALYST

Gutierrez A., Castaño P., Azkoiti M.J., Bilbao J., Arandes J.M.

University of the Basque Country, Faculty of Science and Technology, Chemical Engineering Department (Leioa, Group CPWV), 48080-644 Bilbao, Spain.
Tel.: +34-94601-8435, Fax: +34-94601-3500, e-mail: pedro.castano@ehu.es

The restrictions of aromatic content in fuels are forcing refiners to find valorization routes for surplus aromatics [1,2]. Pyrolysis Gasoline (PyGas) is a byproduct of the steamcracker and is one of the main sources of aromatics. The hydroprocessing of PyGas over bifunctional catalysts leads to high quality products, i.e. C_{2+} *n*-alkanes and isoalkanes, which at the same time can be re-circulated to the steamcracker or used in the gasoline pool [3]. Based on our previous kinetic modeling of probe molecules as toluene [4] and methylcyclohexane [5], we have developed a single kinetic model for the hydroprocessing of a real-refinery feedstock as PyGas. The model is based on discrete lumping of the hundreds of molecules involved.

The catalyst has been prepared impregnating a solution of Pt and Pd onto a HZSM-5 zeolite (Zeolyst Int.), after impregnation the catalyst has been dried, pelletized and calcined up to 450 °C. Prior to reaction the metals have been activated by direct reduction for 2 h at 400 °C. The hydroprocessing experiments have been carried out in a fixed bed reactor at WHSV= 2.7-32 h^{-1}; 350-450 °C; 20-50 bar; $P_{PyGas=}$1 bar and H_2:PyGas molar ratio (n_{H2}), 20-49. The main properties of the used catalyst are the following: Pt content of 0.2 wt%, Pd content of 0.5 wt% (measured by ICP), surface area of 313 $m^2/g_{catalyst}$ (adsorption-desorption of N_2), metallic dispersion of 54 % (adsorption of CO), acidity of 506 μmol of $NH_3/g_{catalyst}$ and acid strength of 117 J/mmol of NH_3 (DSC-adsorption of NH_3).

Our previous results have shown that as long as the strongly-acid-site (normally associated to Brønsted type) content is high, an increase in the conversion is shown when the pore diameter of the support decrease. By means of CMR [6] index it has been demonstrated that the activity of protolytic cracking is higher for bifunctional catalysts.

For the kinetic interpretation we have lumped the products into six groups of molecules with similar from behavior: aromatics, cycloalkanes, alkenes, isoalkanes, C_{2+} *n*-alkanes and methane. The feedstock (PyGas) is mainly constituted of aromatics (ca. 70 wt. %) but also contains alkenes and cycloalkanes. Coke is also formed on the catalytic surface, however the fraction of PyGas transformed into coke is negligible. Based to our previous knowledge of the kinetic modeling of hydroprocessing of model compounds, a kinetic scheme has been proposed (Figure 1) for the hidroprocessing of PyGas.

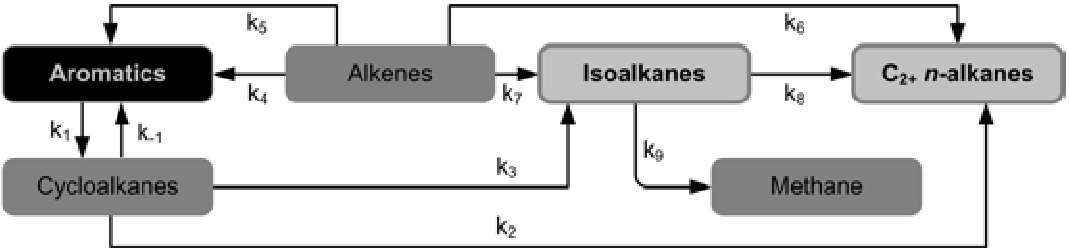


Figure 1. The proponed kinetic scheme for PyGas hydroprocessing over PtPd/HZSM-5 catalyst.

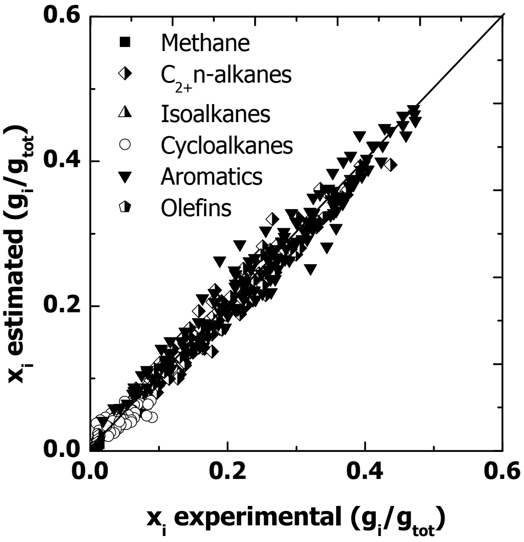


Figure 2. Parity diagram for the proposed kinetic model.

We have observed that the increase of P_{H2} and space time favors the cracking reactions and the hydrogenation of olefins. The temperature favors the C_{2+} *n*-alkane yield while diminishes the isoalkane yield. The parameter estimation has been done by means of an in-house written code based on the *Matlab*'s function *lsqcurvefit* using the large-scale algorithm. The good agreement between the estimated and experimental data is shown in Figure 2.

References

[1] C. Song, X. Ma, *Appl. Catal., B: Environ.* 41 (2003) 207.
[2] R.G. Tailleur, J. Ravigli, S. Quenza, N. Valencia, *Appl. Catal., A: Gen.* 282 (2005) 227.
[3] J. Weitkamp, A. Raichle, Y. Traa, *Appl. Catal., A: Gen.* 222 (2001) 277.
[4] P. Castaño, J.M. Arandes, B. Pawelec, M. Olazar, J. Bilbao, *Ind. Eng. Chem. Res.* 47 (2008) 1043.
[5] P. Castaño, A.G. Gayubo, B. Pawelec, J.L.G. Fierro, J.M. Arandes, *Chem. Eng. J.* 140 (2008) 287.
[6] P. Castaño, B. Pawelec, J.L.G. Fierro, J.M. Arandes, J. Bilbao, *Appl. Catal., A: Gen.* 315 (2006) 101.

COMBINED TECHNOLOGY OF UTILIZATION OF SO_2 FROM WASTE GASES RELEASED BY ANODE PRODUCTION OF ALUMINIUM PLANTS

Pai Z.P. and **Simonov A.D.**

Boreskov Institute of Catalysis SB RAS,
Prosp. Akad. Lavrentieva, 5, Novosibirsk 630090, Russia
Fax: (383) 326 95 67, E-mail: zpai@catalysis.ru

The development of new technologies for deep cleaning of industrial gases from toxic admixtures is an actual problem. Over a long period, the researches on the development of gas- and liquid-phase processes for cleaning of industrial gases from different toxic pollutants, such as SO_2, H_2S, NO_x, As_2O_3, HCN etc. have been carried out in the Boreskov Institute of Catalysis [1, 2]. In particular, it was suggested to purify gas flows resulting from the coke calcination on the production of anode mass for aluminum plants by a combined technology of utilization of sulfur dioxide with the production of sodium sulfate as a commercial product. On the production of anode mass, the combustion of mazut (containing up to 4% of sulfur) yields a considerable quantity of sulfur dioxide (about 7 000 mg/nm^3).

The suggested technology includes the following stages:

1. Dry adsorption-catalytic cleaning of gas;
2. Liquid-phase cleaning of gas.

After a calcination furnace (1), an effluent gas flow is directed to a waste-heat boiler (2), where the gas is cooled to 250-300°C, and then directed to the cyclone (3a) to be cleaned from dust. The degree of gas cleaning from dust is 85-90%. Then the gas passes to an adsorber (4) (stage 1) to undergo the dry adsorption-catalytic cleaning. The degree of gas cleaning from sulfur dioxide is 99.0-99.5%. The cleaned gas is discharged into the atmosphere from the cyclone (3b). A reactor-regenerator (5) permits nonstop catalytic regeneration of the adsorbent. The concentrated gas flow is directed from the reactor-regenerator (5) to the cyclone (3c), where it is purified from adsorbent and catalyst particles. Then the gas flow containing sulfur dioxide is directed to a reactor-absorber (6) (stage 2), where the main reactions between sulfur dioxide and sodium hydroxide solution occur to yield sodium sulfate. The purified gas flow from the reactor-absorber 6 meets a gas flow from the cyclone 3b, the combined flow is vented into the atmosphere through a smoke flue. To spray the absorber, a solution is fed from the tank (7). A portion of the solution from the bottom of the absorber (6) is directed to the tank (8) to provide the crystallization of sodium sulfate. The precipitated Na_2SO_4 crystals are filtered from the solution by a filter (9) and directed to a drier (10) to obtain anhydrous salt. The main absorbent volume is in the recycle of stage 2. The flows running from the crystallizer (8), the filter (9) and the drying apparatus (10) are also directed for recycling.

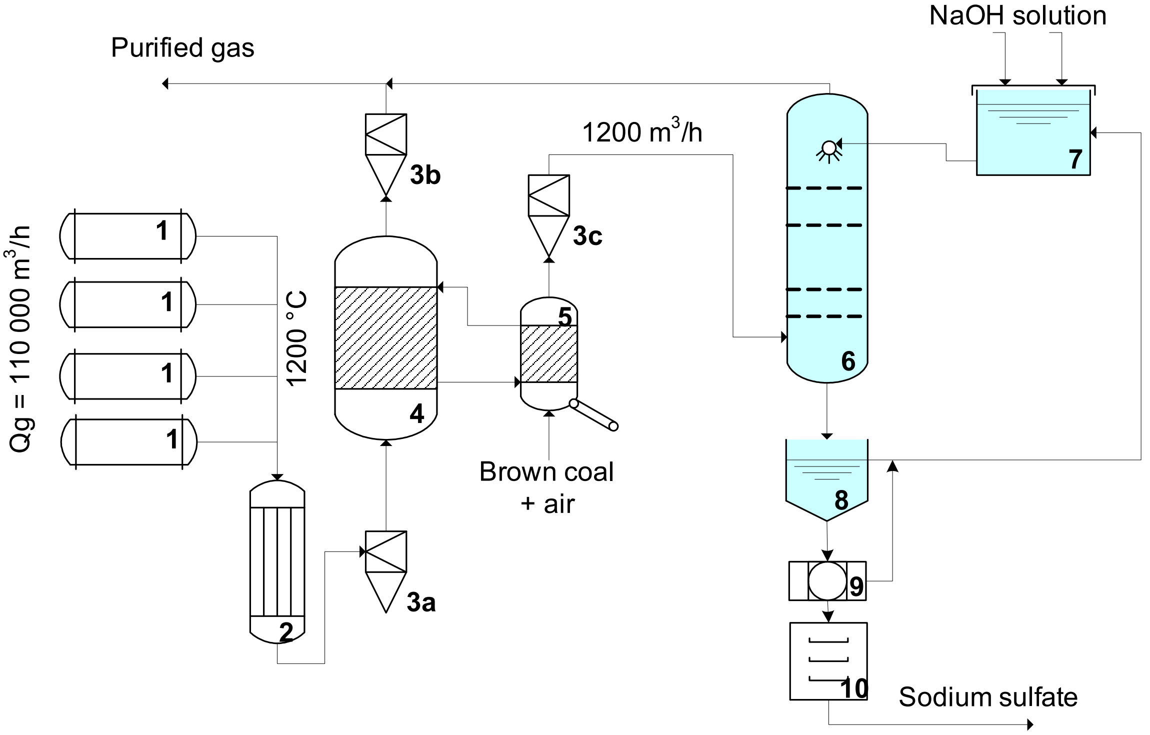


Fig. 1. Scheme of the plant for purification of gases yielding from the furnaces of coke calcination and simultaneous utilization of sulfur dioxide as sodium sulfate.

1. Calcining furnace; **2.** Waste-heat boiler; **3a, 3b, 3c** Cyclone; **4.** Adsorber; **5.** Reactor-regenerator; **6.** Reactor-absorber; **7.** Tank for solution, **8.** Crystallizer; **9.** Filter; **10.** Drying apparatus.

For the plant Qg = 110000 m^3/h (with respect to purified gas containing 1.0 g/m^3 of SO_2), the weight of adsorbent fed into the adsorber is 25 t, the amount of adsorbent required for regeneration is 5500 kg/h, the weight of catalyst charged into the regenerator is 100 kg, the annual catalyst consumption is 100 kg. The pay-back period of the plant is 4-5 years. It should be noted that if it is required, the suggested technology permits manufacturing of such commercial products as potassium sulfate or ammonium sulfate without any changes in the technology.

References

[1]. Z.P. Pai. Methods of desulfation of industrial waste gases. XIV International Conference-Exhibition «Aluminum of Siberia -2008», 2008, Krasnoyarsk, Russia.

[2]. Z.P. Pai. Sulfur utilization during purification and processing of hydrocarbon feedstock, III Russian Conference «Urgent Problems in Petrochemistry », 2009, Zvenigorod, Russia, pp. 148-149.

OP-III-B-16

MATEMATICAL MODEL FOR DOWNDRAFT BIOMASS GASIFIER IN STEADY STATE

Felipe Orlando Centeno Gonzalez[1], **Electo Eduardo Silva Lora**[1],
Rubenildo Vieira Andrade[1], **René Lesme Jaén**[2]

[1]*Núcleo de Excelência em Geração Térmica e Distribuída – NEST,*
Universidade Federal de Itajubá - (Brazil), fcenteno@ingenieros.com.
[2]*Universidad de Oriente – (Cuba)*

Thermo-chemical gasification is likely to be the most cost-effective process to convert solid fuel into gaseous fuels [1]. In this process the biomass goes into a reactor under a restricted amount of oxygen below the stoichiometric, taking place within it a series of thermochemical processes that result in a mixture of gases. The chemical energy contained within the gas produced depends on its composition. Then, the chemical composition determine fuel quality, high concentration of combustible gases such as H_2, CH_4 and CO increase the energy of combustion of the gas. Among the various types of gasifiers within which can be carried out biomass gasification is the downdraft gasifier, among other things, this is characterized by producing a gas with low particulate [2] allowing the use of it in equipments such as turbines, internal combustion engines, fuel cells, etc. Biomass gasification has emerged as a promising technology to meet energy needs, particularly in remote areas away from mains supply.

During gasification occur four fundamental processes (drying, pyrolysis, oxidation and reduction) and each of these processes are characterized by certain physical and chemical phenomena. In downdraft gasifiers unlike other types of reactors, it was found that these processes occur virtually separated into different areas of the reactor. Several researchers [2-9] take advantage of this peculiarity to divide the mathematical models of downdraft gasifiers in several areas. This paper shows the development of a model of three zones: drying, pyrolysis, oxidation and reduction. The gasifier modeled is a fixed bed downdraft reactor, where biomass enters the top of the reactor, while gas enters a medium height and the gas exits through the bottom of the reactor.

The upper submodel corresponds to the phenomena of drying and pyrolysis together, in this area biomass enters the top, as the temperature increases the moisture is being released and then thermal decomposition occurs, resulting char, water vapor and a series volatile species (CO, CO_2, H_2, CH_4 and C_2H_2)[8]. Products leaving the first area (drying - pyrolysis) to enter the zone of oxidation, also enters the air; combustible gases react with available oxygen from the air in and out as products: char, tar e a mix of gases (CO, CO_2, H_2, CH_4, H_2O and N_2) including nitrogen from the air, considered inert and water vapor [2-3]. In the bottom of the reactor is the reduction zone, also known as gasification zone. Entering this zone products of oxidation zone and react with them according to four simultaneous reactions, resulting in a greater concentration of combustible gases. Here the nitrogen and tar are considered inert. The gaseous products of this area are (CO, CO_2, H_2, CH_4, H_2O and N_2) [2-3].

The model is able to predict the profile of molar concentrations of species and the temperature profile in the gasifier, which are useful design parameters for material selection and sizing of reactor. The results obtained with this model are in good agreement with data obtained with other models and experimental data from previous research published in the literature.

References

[1]. Y. Lu, L. Guo, X. Zhang, Q. Yan, Thermodynamic modeling and analysis of biomass gasification for hydrogen production in supercritical water, Chemical Engineering Journal, 131 (2007) 233-244.

[2]. D.L. Giltrap, R. McKibbin, G.R.G. Barnes, A steady state model of gas-char reactions in a downdraft biomass gasifier, Solar Energy, 74 (2003) 85-91.

[3]. D.L. Giltrap, Investigating Downdraft Gasification of Biomass, in: Institute of Fundamental Sciences, Masssey University, Palmerston North, New Zealand, 2002, pp. 156.

[4]. T.H. Jayah, L. Aye, R.J. Fuller, D.F. Stewart, Computer simulation of a downdraft wood gasifier for tea drying, Biomass and Bioenergy, 25 (2003) 459-469.

[5]. N. Gao, A. Li, Modeling and simulation of combined pyrolysis and reduction zone for a downdraft biomass gasifier, Energy Conversion and Management, 49 (2008) 3483-3490.

[6]. A.K. Sharma, Equilibrium modeling of global reduction reactions for a downdraft (biomass) gasifier, Energy Conversion and Management, 49 (2008) 832-842.

[7]. A.K. Sharma, Equilibrium and kinetic modeling of char reduction reactions in a downdraft biomass gasifier: A comparison, Solar Energy, 82 (2008) 918-928.

[8]. J.K. Ratnadhariya, S.A. Channiwala, Three zone equilibrium and kinetic free modeling of biomass gasifier - a novel approach, Renewable Energy, 34 (2009) 1050-1058.

[9]. J.K. Ratnadhariya, S.A. Channiwala, Two zone equilibrium and kinetic free modeling of gasifier, in: 12th European Conference and Technical Exhibition on Biomass for Energy, Industry and Climate Protection, Amsterdam, The Netherlands, 2002, pp. 813-816.

Acknowledgements

The authors would like to thank Dr. Donna Louise Giltrap for clarifying questions regarding his original model of the area reduction. The financial support of the scholarship program of CAPES is also gratefully.

CATALYTIC DEHYDRATION OF BIOETHANOL TO ETHYLENE: PILOT-SCALE STUDIES AND PROCESS SIMULATION

Kagyrmanova A.P., **Chumachenko V.A.**, **Korotkikh V.N.**,
Kashkin V.N., **Noskov A.S.**

Boreskov Institute of Catalysis of SB RAS, Pr. Lavrentieva, 5,
Novosibirsk, 630090, Russia, aigana@catalysis.ru

Ethylene is a basic product for many applications in the petrochemical industry. The steam cracking process, which employs petroleum fractions and natural gas liquids as feedstocks, is a dominant method for large-scale ethylene production worldwide. Due to increasing of oil prices, bio-ethanol dehydration process could be regarded as cost competitive to steam cracking and a promising technology in producing high purity ethylene from renewable biomass resourses [1].

In this work the process of ethylene production by bio-ethanol dehydration over alumina oxide catalysts has been studied at multiscale approach.

Catalyst screening and activity testing of BIC proprietary and commercial alumina-based catalysts in the reaction of ethanol dehydration have been resulted to a selection of highly active samples with low selectivity towards undesirable by-products such as diethyl ether, butylene and acetaldehyde. Kinetic studies were conducted in a differential reactor over potentially interesting alumina-based catalysts at normal pressure and within temperature interval of 370-450°C. This enabled to determine the reaction networks, to estimate parameters of the kinetic model, and to find the optimal conditions that provides the maximum ethylene yeild.

To study the influence of operation conditions and determine the optimal technological regimes in the unit of an industrial multi-tubular packed

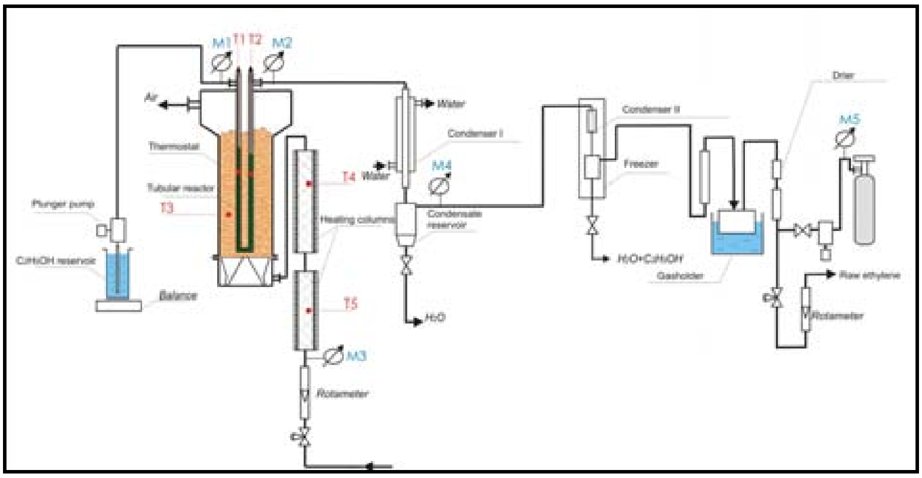


Fig. 1. Sketch of the pilot set-up.

bed reactor, pilot experiments in a single-tube reactor set-up (**Fig.1**) and its mathematical modeling have been carried out.

Pilot reactor testing has been performed with two different catalyst batches by varying process parameters, viz. thermostat temperature, gas flow rate, and residence time in catalyst bed. Effect of the process parameters on the ethanol conversion, the amount and composition of by-products formed in the reaction has been studied. The index C of ethanol consumption per unit of raw ethylene has been determined.

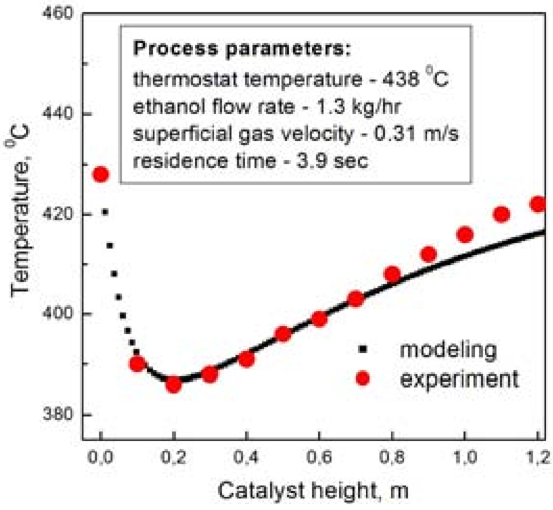


Fig. 2. Comparison of measured and simulated temperature profiles in tubular reactor.

The results obtained show that the lowest index C=1.75 can be achieved when ethanol conversion is less than 98%, and thermostat temperature does not exceed 440°C. At the above conditions the catalysts exhibited good performance and stability.

A two-dimensional pseudo-homogeneous model of a catalyst bed incorporating with a dusty-gas model of a catalyst particle was used for mathematical modeling of the process [2]. The simulated temperature profiles and data on ethanol conversion and product selectivities were in a good agreement with ones observed in pilot experiments (**Fig.2**, **Table 1**). Considering this fact, the model has proved the applicability in design and optimization of the industrial multi-tubular packed bed reactor for ethylene production. As a result, the optimal process parameters in industrial tubular reactor for bio-ethanol dehydration to ethylene over alumina-based catalysts have been determined.

Table 1 Experimental and modeling data in the pilot tubular reactor of ethylene production

Parameter	Experiment	Modeling
Ethanol conversion (%)	98.9	98.5
Ethylene selectivity (%)	98.6	98.8
Acetaldehyde selectivity (%)	0.17	0.26
Diethyl ether selectivity (%)	0.11	0.21
Butylenes selectivity (%)	1.1	0.9

References

[1]. A. Morschnacker, J. Macromol. Sci.// Polym. Rev., 2009, vol. 49:2, p.79-84.

[2]. A.P. Kagyrmanova, I.A. Zolotarskii, E.I. Smirnov, N.V. Vernikovskaya, Chem. Eng. J., 2007, vol.134, p.228-234.

SYNGAS AND HYDROGEN PRODUCTION IN A VOLUMETRIC RADIATION BURNER

Arutyunov V.S., **Shmelev V.M.**, **Sinev M.Yu.**, **Shapovalova O.V.**

Semenov Institute of Chemical Physics, Russ. Acad. Sci.,
Kosygina 4, Moscow, 119991, Russia, arutyunov@center.chph.ras.ru

Introduction

Steam and steam-oxygen reforming of natural gas are routinely used in industrial practice to produce synthesis gas (syngas) and hydrogen. The economical efficiency of these processes sharply falls at decreasing scale of production, so the possibility of their use in low-scale installations required for on-site utilization of natural and associated petroleum gases to prevent their loss or flaring on gas wells and oil fields is doubtful. Also, they can hardly be used for distributed production and supply networks of hydrogen for future transportation needs.

The use of radiation burners based on flat permeable matrixes allows one to improve the efficiency of gas combustion due to a substantially decreasing flame front temperature and, consequently, formation of nitrogen oxides. However, the conversion of chemical energy to intense IR radiation in such open system leads to the increasing loss of energy from the combustion zone and, as a result, to a narrowing of the combustion limits. The latter hampers the hydrocarbon oxidation at high fuel-to-oxygen ratios, at which the formation of syngas (H_2 and CO) can take place. In the case of deep volumetric (3D) matrixes, the combustion proceeds in their cavities in the conditions of partially (or almost fully) locked IR radiation, that leads to substantial decreasing energy losses by radiation and thereby widening the combustion limits in the areas of both fuel lean [1] and fuel rich [2] mixtures.

In this work, the possibility of syngas and hydrogen production based on the natural gas (methane) oxidative conversion at high methane-to-oxygen ratios in a volumetric permeable matrix in the conditions of locked IR radiation is demonstrated.

Experimental part

The experiments were performed in a 3D burner with a rectangular cavity (internal cross-section 80x40 mm, depth 115 mm). Matrix walls and bottom were fabricated from perforated 15-mm-thick ceramic tiles with cylindrical channels of 1.2 mm diameter. The ratio of the total channel cross-section area to the tile area was

0.25. All experiments were performed at atmospheric pressure with a pre-mixed methane-air feed; in order to change the fuel-to-oxygen ratio, methane flow rate was varied at constant air flow rate (35 l/min). The content of carbon oxides and oxygen in the reaction mixture was monitored by a permanent gas analyzer; periodically the mixture composition (H_2, O_2, N_2, CH_4, CO, CO_2) was analyzed using a CG equipped with a TC detector and two packed columns (molecular sieves 13X and Porapak Q).

Results

It was found that being oxidized in the 3D burner, methane can be efficiently converted into a H_2- and CO-containing gas mixture. A stable oxidation is taking place in a wide range of O_2/CH_4 ratios. An example of concentration trends of the main reaction products and methane at varied oxygen-to-methane ratio is presented on Fig.1. Concentrations of H_2 and CO decrease at increasing oxygen content in the initial mixture, whereas CO_2 content increases. The comparison with the results of adiabatic thermodynamic calculations demonstrates that the measured values are very close to calculated ones: at $[O_2]_0/[CH_4]_0$ = 0.8 and almost total oxygen consumption hydrogen concentration varies from 18 to 22 % and CO - from 11 to 14 % at equilibrium values ~25 and ~14%, respectively. CO_2 concentration approaches its equilibrium value at high $[CH_4]_0$. A treatment of the tile walls with active catalytic components leads to a significant widening of the combustion limit for methane-rich mixtures.

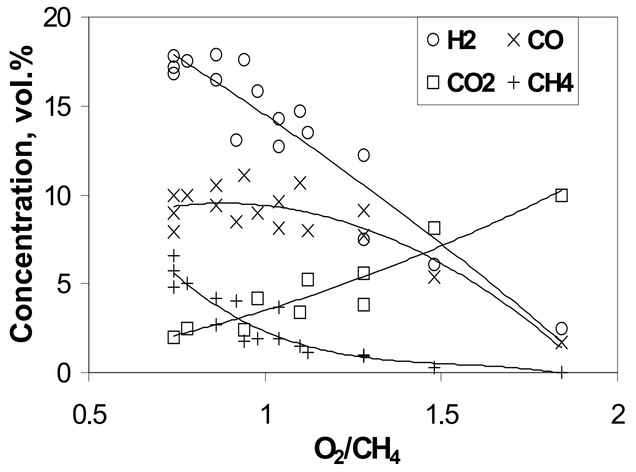


Fig. 1. Concentrations of components in the outlet gas vs.initial oxygen-to-methane ratio.

Thus, the combustion of natural gas (methane) in volumetric permeable matrix burners in the conditions of locked infrared radiation can be considered as a high-production and adaptable way of syngas and hydrogen production for various low scale applications.

References

[1]. V.M. Shmelev and A.D. Margolin. Khim. Fiz., 2000, Vol. 19, No. 5, p. 36.

[2]. V.S. Arutyunov, V.M. Shmelev, I.N. Lobanov, and G.G. Politenkova. Theor. Found. Chem. Eng., 2010, Vol. 44, No. 1, p. 20.

POSTER PRESENTATIONS

SECTION I

PP-I-1

HYDRODYNAMICS OF TAYLOR FLOW OF GAS-LIQUID SYSTEMS IN MICRO CHANNELS: THEORY AND EXPERIMENT

Abiev R.Sh., **Lavretsov I.V.**

St. Petersburg State Technological Institute (Technical University),
St. Petersburg, Russia, abiev_r@mail.ru

In last two decades micro technologies and micro equipment are the objects of great interest, in the first place for mixing, heat transfer, extraction, as chemical reactors for organic and inorganic reactions, as well as lab on a chip for chemical or biological analysis. Most apparatuses for such processes consist of one or many micro channels with hydraulic diameter in range 0.3 - 2 mm. It has been revealed that the most effective flow mode for mass transfer is Taylor flow (slug or plug flow). The mass transfer rate depends on some hydrodynamic parameters like capillary number, bubble velocity and length, liquid slug length etc.

In our papers [1-3] a mathematical model (1)-(7), including Aussilous-Quere equation (7), for the gas–liquid slug flow in a capillary is developed (indices "1" and "2" correspond to liquid and gas).

$$\rho\left(\frac{\partial u_x}{\partial t}+u_r\frac{\partial u_x}{\partial r}+\frac{u_\theta}{r}\frac{\partial u_x}{\partial \theta}+u_x\frac{\partial u_x}{\partial x}\right)=-\frac{\partial}{\partial x}\left(p-\rho g_x x\right)+\mu\nabla^2 u_x, \tag{1}$$

$$\frac{\partial \rho}{\partial t}+\frac{\partial(\rho u_r r)}{r\partial r}+\frac{\partial(\rho u_\theta)}{r\partial \theta}+\frac{\partial(\rho u_x)}{\partial x}=0, \tag{2}$$

$$\tau_2\big|_{r=0}=\mu_2\left(\frac{\partial u_x}{\partial r}+\frac{\partial u_r}{\partial x}\right)=0, \quad (3) \qquad u_1\big|_{r=R}=0\ , \quad (4)$$

$$u_1\big|_{r=R_b}=u_2\big|_{r=R_b}\ , \quad (5) \qquad \tau_1\big|_{r=R_b}=\tau_2\big|_{r=R_b}\ , \quad (6)$$

$$\frac{\delta}{R}=\frac{1.34\cdot \mathrm{Ca}^{2/3}}{1+3.35\cdot \mathrm{Ca}^{2/3}}. \tag{7}$$

Using the mathematical model (1)-(7) the velocity profiles in the bubble, film, and liquid slugs are calculated. The experimentally found bifurcational behavior of the slip velocity of bubbles relative to the two-phase mixture reported in the literature is described and supported by the theory. The boundaries of the existence of bypass and circulation modes of slug flow past bubbles are theoretically substantiated. The influence of the direction of a gas–liquid flow on the velocity of bubbles is explained. The value of a critical capillary number predicted by Taylor for a horizontal capillary (0.707) is theoretically confirmed.

A method for calculating the void fraction and relative size of bubbles at the known flow rates of phases is constructed using the mathematical model (1)-(7). It is shown that the void fraction depends not only on the dynamic gas holdup, but also on the capillary number and the Weber number, as well as on the direction of the flow.

The calculated results are in good agreement with the experimental data of other researchers [4, 5].

Our experimental set-up consisted of horizontal glass capillary with a length 355 mm and inner diameter 0.92 mm; injection needle for gas inlet to capillary. Gas flow rate is regulated by needle valve and measured by Honeywell AWM 43300V sensor. Liquid is delivered by peristaltic pump Heidolph PD5206. Pressure drop in two points of capillary – entrance and exit is measured by Elemer AIR-20M5 sensors. Pressure losses were taken into account in further data processing. Liquid slug length and bubble length were estimated by photography with Nikon D60 body and Nikon DX AF-S Nikkor 18-55 mm lens (exposure 1/125 s, photo size 3872x2592 pix, length of single bubble was more than 24 pix).

Two infrared sensors are used to define gas bubble velocity. There is 230 mm between inlet to capillary and first infrared sensor. Signals from sensors were converted from analog to digital for further processing on the computer. Then we can calculate gas bubble velocity knowing time difference between two signals that are processed with correlate function. Experiments were conducted in air-water and air-glycerin systems. Set-up construction and tolerance of our instruments are made possible to carry out experiments for liquid 0.17 – 0.73 m/s and air 0.09 – 0.56 m/s. Obtained experimental data are in good agreement with our theoretical model.

References

[1]. Abiev, R.Sh., Simulation of the Slug Flow of a Gas–Liquid System in Capillaries, *Theor. Found. Chem. Eng.*, 2008, vol. 42, no. 2, p. 105.

[2]. Abiev, R.Sh., Circulation and By-Pass Modes of the Slug Flow of a Gas–Liquid Mixture in Capillaries, *Theor. Found. Chem. Eng.*, 2009, vol. 43, no. 3, p. 298.

[3]. Abiev, R.Sh., Method for Calculating the Void Fraction and Relative Length of Bubbles under Slug Flow Conditions in Capillaries, *Theor. Found. Chem. Eng.*, 2010, vol. 44, no. 1, p. 86.

[4]. Kreutzer, M.T., Kapteijn, F., Moulijn, J.A., et al., Inertial and Interfacial Effects on Pressure Drop of Taylor Flow in Capillaries, *AIChE J.*, 2005, vol. 51, p. 2428.

[5]. Liu, H., Vandu, C.O., and Krishna, R., Hydrodynamics of Taylor Flow in Vertical Capillaries: Flow Regimes, Bubble Rise Velocity, Liquid Slug Length, and Pressure Drop, *Ind. Eng. Chem. Res.*, 2005, vol. 44, p. 4884.

PP-I-2

ESTIMATION OF EFFICIENCY OF DIRECT-FLOW HASHING

Afanasenko V.G., **Nikolaev Y.A.**

Ufa State Petroleum Technological University, Ufa, Russia

Agitation is extensively used in a chemical and a related branches of industry for preparation of emulsions, suspensions, homogeneous systems, and also for enhancing the chemical, heat, and diffusive processes.

Let us consider the agitation as a way for enhancing the chemical, heat, and diffusive processes in the homo- and heterogeneous systems. These processes are applied to absorption, evaporation, extraction, and other chemical technologies because a good mixing of components provides optimum conditions for feeding the substances to a reaction area, an interphase boundary or a heat exchange surface. The enhancing of exchange processes is performed primarily due to [1]:

- increase of phase contact area;
- increase in the speed of relative movement of phases;
- use of nonsteady regimes of an interphase exchange that provide reaching high instantaneous values of mass transfer coefficients;
- executing the mass exchange in hydrodynamically unstationary conditions of the interphase surface.

Ways and selection of devices for agitation are determined by a target of agitation and an aggregate state of mixed materials. The agitation in the liquid media is extensively used in chemical industry [2].

Direct flow mixing of components for concentration equalizing on a cross sectional area normal to a velocity vector is one of the agitation ways in the fluid media. For estimation of an operation efficiency of such devices analogously to mechanic agitators the following characteristic features can be marked:

- energy loss;
- intensity or degree of the agitation;
- agitation efficiency.

ENERGY LOSS

The energy loss of a mechanical agitators is expressed by the driver power consumption that reveals the amount of spent energy for an overcoming the friction force of the agitator blades against a liquid.

In a case of the direct flow agitation a pressure drop on the agitation section of the device including the feed area, the agitator, and an area of stabilizing movement can be assumed as parameter defining the energy loss.

At the agitation of the liquid components in a pipe of the constant cross section the pressure dropped owing to hydrostatic constituent and therefore the energy loss is characterized only by the pressure drop.

THE INTENSITY OF THE AGITATION

Usually the intensity of the agitation is defined by time of reaching the given technological result or at the mechanical mixing by the speed of the agitator at a given duration of the process. The agitation intensity is the higher the smaller is the time spent for reaching of the given agitation result. The enhancing of the agitation results in the decrease of the designing devices and in an output rise. It is required from the economic point of view that the target agitation is reached in the shortest time.

A quantitative estimation of the agitation intensities of the direct flow agitators should be related to the the given agitation result. The enhancing of the agitation results in the decrease of the designing devices and in an output rise. It is required from the economic point of view that the target agitation is reached in the shortest time.

A quantitative estimation of the agitation intensities of the direct flow agitators should be related to the geometric size of the device. Thus in the pipe of round cross section the agitation intensities can be described by a relation if the pipe diameter to the length of the mixing device section.

THE AGITATION EFFICIENCY

The agitation efficiency of the device expresses the quality of the mixing operation.

For estimation of the agitation efficiency in the general case a dispersion of concentration that is equaled to standard mean square deviation of concentration from an average concentration should be determined [1]:

$$\sigma(t)=\frac{1}{V}\int_V \left(C(t)-C_{cp}\right)^2 dV\,, (1)$$

where the average concentration is calculated in accordance with:

$$C_{cp}=\frac{1}{V}\int_V C\,dV\,. (2)$$

For the direct flow agitators the efficiency of the mixing described by the concentration dispersion in an area normal to the velocity vector after the mixing section S:

$$\sigma(x)=\frac{1}{S}\int_S \left(C-C_{cp}\right)^2 dS\,, (3)$$

where the average concentration is calculated according to:

$$C_{cp}=\frac{1}{S}\int_S C\,dS\,. (4)$$

Deriving the general criterion for the estimation of the efficiency of the direct flow agitator is complicated by considerable distinctions in physicochemical properties of the mixed components and in the requirements to the agitation efficiency for the optimum process operation. The simplest way to compare various devices is to determine a relation of the agitation efficiency to the energy loss for each device at the satisfaction of the requirements of the process to the intensity and efficiency of the agitation.

Thus selection of the apparatus that appropriates to process execution in the optimum way can be made by comparison of the basis parameters describing the direct flow agitator.

USED DESIGNATIONS

σ is the dispersion of concentration;
t is the time, s;
C is concentration in the considered point;
C_{av} is the average concentration;
V is the volume of the mixing section, m^3;
S is the cross sectional area of the apparatus, m^2;
x is the longitudinal coordinate, m;
Q_1, Q_2 are the volume flow, m^3/s.

References

[1]. Sister, V.G. and Martynov, Yu.V., *Printsipy povysheniya effektivnosti teplomassoobmennykh protsessov* (Bases of Enhancing the Efficiency of the Heat and Mass Exchange), Kaluga: Izd. N. Bochkorevoi, 1998.

[2]. Tsibrovskii, Ya.N., *Osnovy protsessov khimicheskoi tekhnologii* (Bases of the Chemical Engineering), Leningrad: Khimiya, 1967.

NOLINEAR PHENOMENA IN CATALYTIC REACTIONS WITH A BRANCH-CHAIN MECHANISM OF FORMATION OF ACTIVE CENTERS

Andrianova Z.S., Ivanova A.N., and Barelko V.V.

Institute of Problems of Chemical Physics, RAS, Chernogolovka, 142432 Russia,
e-mail: ivanova@icp.ac.ru

This study continues a series of works [1–5] on the special features of instability manifestations in exothermic heterogeneous catalytic reactions with nonlinear kinetics. Here we consider a model of a branched chain catalytic reaction C→ B whose kinetic is described by the scheme

$$C + 2n \rightarrow C_{nn}, \qquad (1)$$

$$C_{nn} + n^* \rightarrow B + 3n, \qquad (2)$$

$$n \rightarrow n^*. \qquad (3)$$

Here, stage (1) corresponds to the two-center adsorption of the initial reagent (C) from the gas phase on surface active centers (n), stage (2) is the formation of the final transformation product (B) accompanied by the multiplication of active centers (n* is the inactive center activated by the catalytic event), and stage (3) describes the reversible deactivation of surface active centers and restoration of their activity.

The accepted physical model corresponds to a thin catalytic filament with a cross flow of reagents past it. Such a model not only simplifies analysis by using the one-dimensional approximation but also corresponds to real conditions of electrothermographic experiments performed to study the dynamic characteristics of heterogeneous catalytic transformations (see [6, 7]). The differential equations describing the system under consideration have the form

$$\begin{aligned}
&m\,\partial T/\partial t = \lambda\,\partial^2 T/\partial x^2 + a/d\Big(\sum_j Q_j W_j - \alpha\left(T - T_0\right)\Big)\\
&\partial c/\partial t = D_c\,\partial^2 c/\partial x^2 + b/\delta\left(-K_1 n^2 c + \beta\left(c_0 - c\right)\right)\\
&\partial n/\partial t = D_n \partial^2 n/\partial x^2 - 2K_1 n^2 c + 3K_2 c_{nn} n^* - K_3^+ n + K_3^- n^* \qquad (4)\\
&\partial n^*/\partial t = D_{n^*}\partial^2 n^*/\partial x^2 - K_2 c_{nn} n^* + K_3^+ n - K_3^- n^*\\
&\partial c_{nn}/\partial t = D_{c_{nn}}\partial^2 c_{nn}/\partial x^2 + K_1 n^2 c - K_2 c_{nn} n^*
\end{aligned}$$

the boundary conditions for the all the $y = (T, c, n, n^*, c_{nn})$ components were introduced by setting the gradient at the ends of a catalytic element at zero.

This model describes a hysteresis temperature dependence of reaction rate, domain structures appear because of local disturbances in the case of diffusion instability of uniform stationary states under certain conditions for transfer coefficients, autowave transition processes are characterized by a “plateau” of zero front velocities with the formation of standing waves.

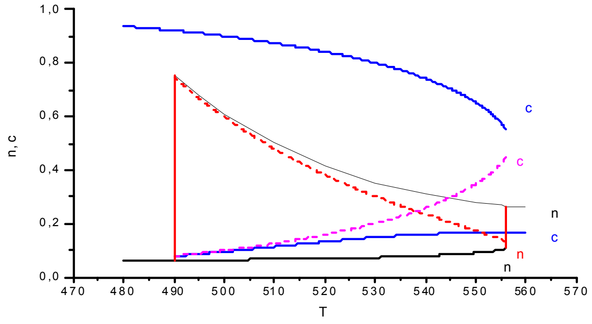


Fig. 1. Bifurcation diagram under isothermal conditions. Dashed lines correspond to unstable states. Bifurcation transitions are marked by vertical lines corresponding to jumps upward for n at T^0=555K and downward at T^0= 490 K.

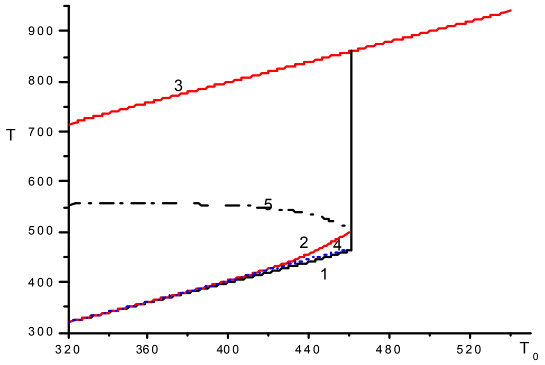


Fig. 2. Bifurcation diagram under non isothermal conditional. Line 2 corresponds to intermediate stable state, lines 4 and 5, to unstable states (1) and (3) are the kinetic and diffusion regimes, respectively.

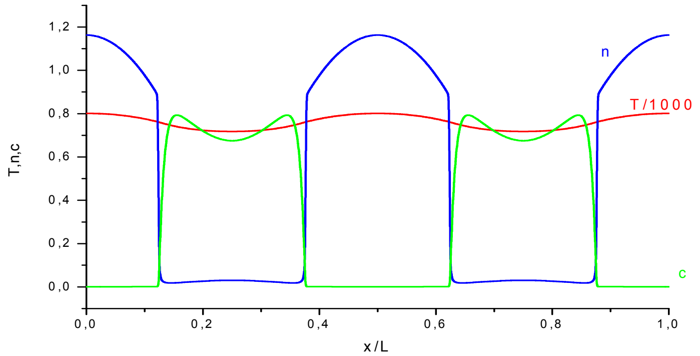
At the initial parametric point:

$$K_{10}=1.176\cdot10^{7}\cdot1/s, E_1=10000kl, K_{20}=4736\cdot1/s, E_2=0, K_{30}^{+}=7.055\cdot10^{5}\cdot1/s,$$

$$E_3^{+}=10000kl, K_{30}^{-}=5.53\cdot10^{8}\cdot1/s, E_3^{-}=20000kl, \beta=20\cdot1/s$$

the system under isothermal conditions at T^0=500K has three stationary points saddle and two stable (nodes),one of which diffusion unstable. Proceeding from this parametric point and varying the α and T^0 parameters had been found all the stationary states. The ones shown on bifurcation diagrams (Fig.1 and Fig. 2).

The instability of uniform stationary states with respect to local perturbations results in the appearance of no uniform structures because of the development of random perturbations.



The Fig.3 shows domain structure at α=0.1 and T^0=500K, D_n=10^{-3}cm^2/s, D_{n*}=10^{-2}cm^2/s, D_{cnn}=0.1cm^2/s, $\lambda/c_v\rho$=0.2 cm^2/s.

References

[1]. A. I. Ivanova, Z. S. Anrdianova, and V. V. Barelko,Dokl. Akad. Nauk 386, 789 (2002).

[2]. A. I. Ivanova, Z. S. Andrianova, and V. V. Barelko,Khim. Fiz. 23 (1), 73 (2004).

[3]. V.V. Barelko, Z.S. Andrianova, A.N. Ivanova,A.F. Vyatkin, and V.V. Starkov, Dokl. Akad. Nauk 404,1 (2005).

[4]. V. V. Barelko and A. G. Merzhanov, in Problems of Kinetics and Catalysis, Ed. by O. V. Krylov (Nauka,Moscow, 1978), vol. 18, p. 182 [in Russian].

[5]. V. V. Barelko, in Problems of Kinetics and Catalysis, Ed. by O. V. Krylov (Nauka, Moscow, 1981), vol. 18, p. 61 [in Russian].

This work is supported by RFBR, project No 09-08-12041-ofi_m

A NEW APPROACH TO KINETIC STUDY OF PALLADIUM-CATALYZED SYNTHESIS OF VINYL ACETATE IN A HETEROGENEOUS GAS REACTION AND EFFECTS OF ALKALI METALLIC ACETATE PROMOTERS

Arjmand M.[1], **Motahari K.**[2], **Atashi H.**[3]

[1]*Royal Institute of Technology (KTH), Graduate School of Chemical Engineering,*
E-mail: arjmand@kth.se
[2]*Arak University, Department of Chemical Engineering, Arak, Iran*
[3]*Zahedan University, Department of Chemical Engineering, Zahedan, Iran*

1. Introduction

Vinyl acetate (VA) has been commercially prepared from ethylene (C_2H_4), acetic acid (AcOH) and oxygen. The ideal reaction pathway is

$$C_2H_4 + CH_3COOH + \frac{1}{2}O_2 \rightarrow C_2H_3OOCCH_3 + H_2O$$

So far various experimental investigation into finding the reaction kinetics [1-3] and mechanism have been carried out. However the work on analysis and study of promoters on this case is still limited. Herein, by injection of different promoters, we will be able to determine the surface reaction parameters as well as most effective result.

2. Experimental

All experiments were performed using a plug flow system. A reactor consisting of a 1.5in inner diameter (ID) and 30cm length filled with Pd/SiO_2 catalyst of a diameter of 5mm and dispersion of 600 m^2/gr was used at a pressure of 0.9 MPa and a temperature of 413-433 K. C_2H_4 is saturated with Acetic acid and then evaporated using a heater. The saturated gas will then be superheated and then combined with O_2 and N_2. Oxygen gas will be added on a concentration of less than %7 on molecular basis in order to avoid an explosive reaction between ethylene and oxygen. The mixture leaving the reactor is condensed in two to three stages to obtain vinyl acetate in liquid phase and so prepared for analysis. A schematic diagram of the process is shown in Fig.1.

Metallic promoters with assessed compound percentages are injected into the reactor by a micro pump. The inlet and outlet of the reactor is connected to a gas chromatograph; continuously determining the compound percentage of the entering and exiting materials of the reactor. The experiments are performed for lithium, sodium, potassium, rubidium and caesium acetate salts.

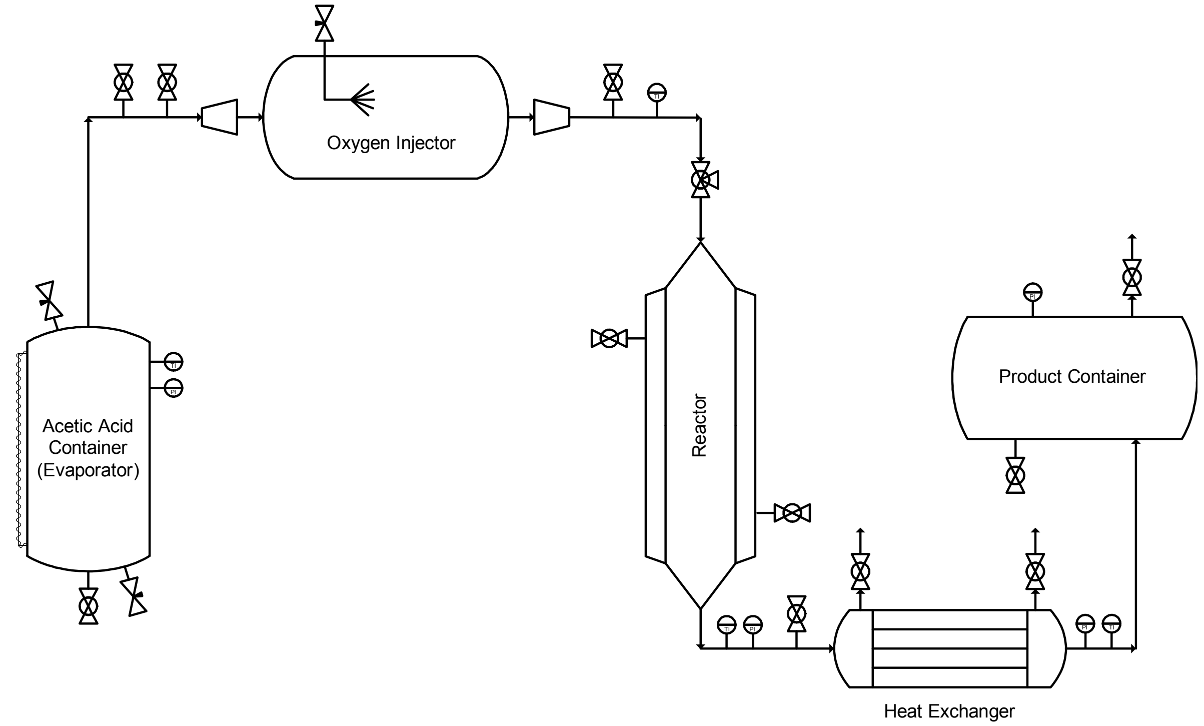


Fig. 1. A schematic of the vinyl acetate pilot reactor instrument

3. Results and Conclusions

The experiments showed that the reaction rate of producing vinyl acetate in presence of Pd-Au catalysts, without implementing promoters can be very slow, thus not economically efficient. However in contrast, metallic promoters increase the reaction rate, eventually increasing the conversion and the selectivity of the reaction by creating an acid layer on the catalyst bed. The acetate salts of alkaline metals such as lithium, sodium and potassium increases the reaction rate significantly while the effect is increased from the top to the bottom of the alkali metals column in the periodic table. To explain this behavior, one can refer to the effect of the common ion. The common ion that is achieved from the dissociation of acetate salts in compounds available on the catalyst bed; improving adhesion of the acetic acid molecules to the catalyst surface, thus producing the mediator material Pd(CH_3CO), which is the main mediator in the production reaction of vinyl acetate on the catalyst bed.

References

[1]. S. Nakamura, T. Yasui, “The mechanism of the palladium-catalyzed synthesis of vinyl acetate from ethylene in a heterogeneous gas reaction”, J. Catal., 17, (**1970**), 366.

[2]. B. Samanos, P. Boutry, R. Montarnal, “The mechanism of vinyl acetate formation by gas-phase catalytic ethylene acetoxidation”, J. Catal., 23 (**1971**), 19.

[3]. A.H. Zaidi, “Catalytic activity of supported liquid-phase lithium—palladium acetate catalysts in the oxidation of ethylene to vinyl acetate”, Appl. Catal., 30 (**1987**), 131.

[4]. Y.F. Han, J.H. Wang, D. Kumar, Z. Yan, D.W. Goodman, "A kinetic study of vinyl acetate synthesis over Pd-Au/Sio2 and Pd/Sio2 catalysts". J. Catal, 232, pp. 467-475 (**2005**).

KINETICS OF PROX REACTION OVER $CuO-CeO_2$ AND CuO CATALYSTS

Avgouropoulos G. and Ioannides T.

Foundation for Research and Technology-Hellas (FORTH), Institute of Chemical
Engineering and High Temperature Chemical Processes (ICE-HT)
P.O. Box 1414, Patras, Greece, E-mail: geoavg@iceht.forth.gr

Introduction

$CuO-CeO_2$ catalysts have been proposed as a promising catalytic system for the preferential CO oxidation in H_2-rich streams (PROX reaction) [1]. The Langmuir-Hinshelwood and Mars-van Krevelen kinetic models have been used to describe the experimental data of CO oxidation on Cu-Ce-O catalysts [2,3]. Transient experiments [4] have favoured the use of redox kinetic model:

Catalyst reduction step: CO or H_2 + oxidized site → reduced site + oxidized products
Catalyst re-oxidation step: O_2 + reduced site → oxidized site

In this work, the results obtained from the kinetic investigation of the reactions of CO and H_2 oxidation and CO_2 inhibition over $CuO-CeO_2$ and CuO catalysts are presented and the effect of CeO_2 on the kinetic parameters is investigated.

Experimental

Kinetic measurements of CO and H_2 oxidation were conducted over a $CuO-CeO_2$ and a pure CuO catalyst (50 mg of powder (90<dp<180 μm) diluted at a 5:1 ratio with inert seasand) synthesized by a citrate-hydrothermal method [1]. The $CuO-CeO_2$ catalyst (Cu/(Cu+Ce)=0.25) was activated at 400°C (S_{BET}=66 m^2 g^{-1}). The CuO catalyst was activated at 300°C (S_{BET}=21 m^2 g^{-1}). The kinetic experiments were carried out under differential conditions (CO or H_2 conversion<5-10%) in the temperature ranges of 50-135°C (CO oxidation) and 140-180°C (H_2 oxidation).

Results and discussion

The kinetic measurements of CO and H_2 oxidation conducted over $CuO-CeO_2$ and CuO catalysts showed that both reactions are practically of zero order with respect to O_2 partial pressure and of positive order with respect to CO or H_2 partial pressure on both catalysts. While the CO oxidation rate became of zero order at $P_{CO} > 0.02-0.03$ atm, the H_2 oxidation rate increased with increase of H_2 partial pressure up to $P_{H2} = 0.7$ atm. Although $CuO-CeO_2$ was ~8 times more active than CuO in CO oxidation, it was actually less active than CuO in H_2 oxidation. That behavior was accompanied by a considerable decrease by 10-20 kJ mol^{-1} in the E_{app}. The kinetic models, which provided the best fit for CO oxidation were the same for both catalysts. More specifically, these were:

(i) the standard redox model, incorporating a reaction order < 0.1 on P_{O2}

$$R = \frac{k_{CO}P_{CO}k_{O_2}P_{O_2}^{n}}{0.5k_{CO}P_{CO} + k_{O_2}P_{O_2}^{n}(1 + K_{CO_2}P_{CO_2})} \qquad (1)$$

(ii) the modified redox model, which assumes a first order dependence on P_{O2} (for surface oxidation) and includes the CO adsorption term:

$$R = \frac{k_{r}K_{CO}P_{CO}k_{O_2}P_{O_2}}{0.5k_{r}K_{CO}P_{CO} + k_{O_2}P_{O_2}(1 + K_{CO}P_{CO} + K_{CO_2}P_{CO_2})} \qquad (2)$$

The same kinetic models were applied in the case of H_2 oxidation. All the equations incorporate the inhibiting effect of CO_2. The heat of adsorption of CO on CuO-CeO_2 was estimated to be 25 kJ mol^{-1}. This value corresponds to CO adsorbed on oxidized sites, since CO adsorption on reduced (Cu^+) sites may also take place, but it does not influence the steady-state reaction rate. The activation energies for the reduction and oxidation steps were found to be higher for the oxidation step (69.6 kJ mol^{-1}) compared to the reduction step (40.6 kJ mol^{-1}). The kinetic parameters of CO oxidation over CuO took lower values than those of the CuO-CeO_2 catalysts, reflecting the lower activity of this catalyst. The most pronounced difference is in the rate constant of the reduction step, k_{CO}, which in the temperature range of 50-100°C is 25 times (at 50°C) or 6.5 times (at 100°C) smaller for the CuO catalyst. The rate constant of the oxidation step, k_{O2}, in CuO, on the other hand, is 3-4 times smaller in the same temperature range. This implies that CeO_2 promotes to a greater extent the reduction of copper oxide species than their reoxidation. The promoting effect of ceria was also revealed in the case of CO_2 inhibition, since the calculated heat of adsorption of CO_2 was twice as large on CuO compared to CuO-CeO_2.

Conclusions

Rate expressions derived from redox (Mars-van Krevelen) mechanisms describe satisfactorily the observed kinetic behavior in PROX reaction. The presence of ceria enhanced the reduction step and improved the tolerance towards CO_2.

References

[1] G. Avgouropoulos and T. Ioannides, Appl. Catal. B 67 (2006) 1.
[2] G. Sedmak, S. Hocevar, J. Levec, J. Catal. 213 (2003) 135.
[3] W. Liu, M. Flytzani-Stephanopoulos, J. Catal. 153 (1995) 317.
[4] G. Sedmak, S. Hocevar, J. Levec, J. Catal. 222 (2004) 87.

PHENOMENA OF SUPERADIABATIC TEMPERATURE IN FLAMES AND SPONTANEOUS IGNITION PROCESSES

Babkin V.S. and **Bunev V.A.**

Institute of Chemical Kinetics and Combustion, Novosibirsk, Russia
e-mail: babkin@kinetics.nsc.ru

The term "superadiabatic temperature" (SAT) implies the phenomena occurring upon combustion with which the temperatures evolve that are superequilibrium for the given system and conditions in the zone of chemical transformations. Although these phenomena have long been observed, they did not fix much attention of researchers. On the other hand, the phenomena are of interest in terms of the chemical physics of the mechanisms of interaction of elementary processes leading to SAT and are rather promising regarding the present-day technologies. It appeared that the SAT effects in which tens and hundreds of degrees of superequilibrium temperature are attained, can be used to solve the problems of energetics, ecology, fire-and-explosion safety, chemical technology, etc.

Usually, the SAT phenomena result from a competition of the processes of molecular diffusion and heat conductivity, the selective diffusion of fuel and oxidizer, heat transfer in multiphase systems, the interaction between parallel and cross-field thermal conductivities, the appearance of the effects of compressibility, etc. The existence of a great variety of the mechanisms of SAT formation has become evident [1]. Thus, of interest is the formation of SAT in flames and the processes of spontaneous ignition.

This report is a review of the recent results from works devoted to the origin of SAT in flames and upon spontaneous ignition of gaseous systems. The studies in this area have produced intriguing results [2-10]. The SAT effect is observed in ,e.g., the flames of rich hydrocarbon mixtures[2]. In [2], attention was given to the formation of superequilibrium water concentration upon combustion. Therefore, the conclusion was drawn on the origin of SAT due to molecular hydrogen diffusion from a high-temperature zone to the low-temperature one. It was further demonstrated that H_2 is of no importance in SAT formation because of its lower reactivity as compared with hydrocarbon molecules in reactions of water formation in the low-temperature zone [7]. A decisive role in the formation of superequilibrium water concentration belongs to the H atom diffusing from the high-temperature zone to the heating one [7-8]. The other reasons for SAT appearance were also put forward [8]. Thus, the problem arises of the feasible appearance of SAT in the absence of molecular transfer of substance and energy upon, e.g., spontaneous ignition of a combustible mixture. The present work reports results of numerical studies on the processes of spontaneous ignition and spreading of the flames of the rich dimethyl ether/air (CH_3OCH_3/air) mixtures at constant pressure and volume [9-10].

It was concluded them that in the processes of spontaneous ignition, a dominating reason of SAT formation is the kinetic competition of the groups of fast and slow chemical reactions. In flames, under temperature and concentration gradient conditions for the participants of the chemical transformation, additional contribution to SAT can be made by the diffusion of intermediates to the low-temperature zone, and, first of all, the diffusion of H atoms. It is shown that the formation of SAT is possible not only in “hot” but also in “cold” hydrocarbon flames [9-10].

The novel data on SAT are of importance both in understanding and predicting the laminar flame propagation limits and in estimating the fire and explosion danger of “cold” flames. They are useful for the analysis of some processes of chemical technology, e.g., for production of syngas and hydrogen, and allow one to answer the question about the systems and conditions in which the formation of SAT is either probable or hardly probable.

References

[1]. V.S. Babkin, I. Wierzba, G.A. Karim, Chem. Eng. J. 91 (2003) 279.
[2]. A.A. Rozlovsky, Dokl. AN SSSR 186 (1969) 373-376 (in Russian).
[3]. F. Liu, H. Guo, G. Smallwood, O. Gulder, Proc. Combust. Inst. 29 (2002) 1543-1550.
[4]. V.V. Zamashchikov, I.G. Namyatov, V.A. Bunev, V.S. Babkin, Combustion, Explosion and Shock Waves 40 (2004) 32-35.
[5]. V.A. Bunev, V.V. Zamashchikov, I.G. Namyatov, V.S. Babkin. Goreniye I Plazmokhimiya.2005, 3, No. 1, p. 1-14 (in Russian).
[6]. F. Liu, O.L. Gulder, Combust. Flame143 (2005) 264-281.
[7]. V.A. Bunev, V.S. Babkin, Combustion, Explosion and Shock Waves 42 (2006) 503-508.
[8]. F. Liu, O. Gulder. Combust. Sci. Technol. 180 (2008) 437-452.
[9]. V.A. Bunev, V.S. Babkin, Mendeleev Commun. 107 (2009) 290-291.
[10].V.A. Bunev, Ekologicheskaya Khimiya 16 (2007) 107-124 (in Russian).

ELECTROMAGNETIC REACTOR OF WATER TREATING FROM OILS AND HYDROCARBONS

Bachurikhin A.L.

Zelinsky N.D. Institute of Organic Chemistry of the Russian Academy of Science,
Russia, Moscow 119991, GSP - 1, the Leninscky av., 47,
E-mail: SECRETARY@ioc.ac.ru

The problem of clearing of water resources from oil pollution is rather actual now. Annual total emission of mineral oil in the seas and oceans as a result of consequences of extraction and emergencies is estimated on different sources, including the National academy of sciences the USA on the average from 6 up to 8 million tons. Nevertheless, the problem of operative and effective liquidation of consequences of similar emissions is far from the decision in view of low efficiency of existing technological decisions, and including, absence high-efficiency the reactor equipment. The majority of known processes of clearing of water environments from oil pollution is based on use the methods of oxidation **[1]**, flotation **[2]**, absorbtion **[3]**, and also methods of biological clearing **[4]**. Under the total characteristics, including productivity, a degree of clearing, simplicity of technological decisions, the economic and power efficiency, the mentioned ways are conditionally suitable for the decision of similar problems.

The clearing process of water environments from oil pollution and dangerous hydrocarbons aromatic and olefinic the lines, based on use is developed and tested in industrial scale as basic reactionary unit of the device of electromagnetic processing water environments. The principle of work is based on the phenomenon of acceleration microparticles association of mineral oil in conditions of interaction of an external variable magnetic field with ferromagnetic sorbent which particles have own constant magnetic field. As a result of such interaction there are intensive association processes the hydrocarbonic components being consequence of concentration in places of impacts of ferromagnetic particles of electromagnetic, thermal and mechanical energies. Further, passing through the polysorbtional layers, the integrated particles of hydrocarbons are absorbed much faster, than similar particles of smaller diameter.

Working parameters of a reactor electromagnetic association:

Initial concentration of mineral oil — 100 ÷ 1 mg/L
Final concentration of mineral oil — 0,5 ÷ 0,05 mg/L
Working volume of a reactor — 30 L
Productivity on initial water — Up to 100 m^3/h
Operating mode — Continuous
Working temperature — 0 ÷ 50°C
Working pressure — 0 ÷ 1,0 MPa

Besides direct use of the specified installation during water treating, there are variants of her modification, allowing her use in a number of adjacent tasks of oil extracting and processing. In particular, her use is planned during preliminary processing, tars, bitumen sand, in manufacture of dyes, etc. spheres.

The general distinctive characteristics of installation:

1) High efficiency
2) Stability to a high level of pollution of communications (a rust, sand, fine stones)
3) Standardization of a design with an opportunity of fast replacement of elements (a grid, a pipe, nozzles and so forth)
4) Absence of a problem of deterioration in case of use the plastic case of a reactor

Installation has passed industrial tests in a zone of the Caspian pool: Russia, Republic Dagestan. On a method of clearing of water environments from mineral oil with participation of the described device the patent of the Russian Federation - №2371232 « THE METHOD OF CLEARING OF THE WATER ENVIRONMENT FROM MINERAL OIL», a priority - from 27.06.2008 is received.

References

[1]. JP 2005246354. WATER PURIFICATION DEVICE TO REMOVE OIL COMPONENT FROM KITCHEN WASTEWATER BY OZONE. Auth. Koyashiki, Kazuo.

[2]. RU Pat. 2075452. The METHOD of SEWAGE TREATMENT of SLAUGHTERHOUSES AND MEAT-PACKING PLANTS. Auth. Zhuravlyov S.G., etc.

[3]. RU Pat. 2077493. METHOD of CLEARING of POTABLE WATER. Gajdadymov V.B., etc.

[4]. RU Pat. 2076150, CLAN BACTERIA ACINETOBACTER SPECIES (BICOCCUM), USED FOR WEEDING AND WATER FROM MINERAL OIL, CLAN BACTERIA ARTHROBACTER SPECIES, USED FOR WEEDING AND WATER FROM MINERAL OIL, CLAN BACTERIA RHODOCOCCUS SPECIES, USED FOR WEEDING AND WATER FROM MINERAL OIL, the METHOD of BIOLOGICAL CLEARING OF OIL POLLUTION (VARIANTS), Auth. Murzakov Boris Gerasimovich, etc.

DIRECT SYNTHESIS OF HYDROGEN PEROXIDE IN BATCH REACTOR: UNDERSTANDING THE KINETICS AND MECHANISMS

Pierdomenico Biasi[1], Jose Rafael Hernandez Carucci[1], Nicola Gemo[2], Kari Eranen[1], Paolo Canu[2], Tapio Salmi[1]

[1]*Process chemistry centre (PCC), Laboratory of Industrial Chemistry and Reaction Engineering Åbo Akademi, Biskopsgatan 8, TURKU 20500 FINLAND,*
E-mail: bpierdom@abo.fi
[2]*Dipartimento di Principi e Impianti di Ingegneria Chimica "I. Sorgato" (DIPIC)*
University of Padova, via Marzolo 9, 35131, PADOVA, Italy

Today, hydrogen peroxide is produced by an indirect process in which an alkyl anthraquinone is sequentially hydrogenated with a catalyst and oxidized. In this way hydrogen and oxygen are kept separated during the manufacturing process. A process where the direct reaction of $H_2 + O_2 \rightarrow H_2O_2$ takes place could be preferred if control of the sequential hydrogenation can be achieved, but none of the current available processes has solved the productivity vs. safety dilemma.

Despite an extensive body of research on the direct synthesis process, there are limited studies were the kinetic rate expressions on the full reaction network are described and verified. Few attempts to obtain rate equations describing the kinetics of the direct synthesis reaction have been made by Voloshin and coworkers [1], Melada and collaborators [2] and Inoue et al. [3] and further development is still needed.

Our goal is to determine the kinetics of the direct synthesis of H_2O_2 in a batch reactor at high pressure, taking in account vapour-liquid equilibrium between gas and liquid phases and adsorption effects in the catalyst surface.

The direct synthesis of hydrogen peroxide from molecular hydrogen and oxygen was performed in a Parr stainless steel batch reactor with a volume of 600 ml and a maximum working pressure of 200 bar with a commercial 5 wt.% Pd/C catalyst (Evonik). Mixing was carried out with a Heidolph RZR 2021 rotor operating at 1000 rpm. During each experiment, the reactor was charged with 0.1 g of catalyst. The varied parameters for kinetic modeling were pressure (10-20 bar), hydrogen and oxygen partial pressures (H_2 0.5-3 bar, O_2 3-8 bar the remaining is CO_2 as inert gas), and temperature (-5, 0 and 10 °C). H_2O_2 and H_2O were measured by iodometric and KF titration.

Experiments carried out under kinetic control revealed that hydrogen peroxide was successfully formed on the catalyst surface, but it was decomposed as the reaction time was prolonged. The mass balances of the components were considered in detail. A Langmuir-Hinshelwood rate mechanism was proposed based on the competitive adsorption of hydrogen and oxygen on the palladium surface. The adsorption and desorption steps are assumed to be rapid enough to reach quasi-equilibria, while the surface reaction steps are assumed to limit the rates. The surface reactions leading to the formation of hydrogen peroxide and water were assumed to be rate determining, after which the rate equations describing the system were derived and the kinetic parameters were estimated by nonlinear regression analysis. The model gave a good fit to the experimental data and it was used to predict the system behaviour under batch conditions (See Fig. 1).

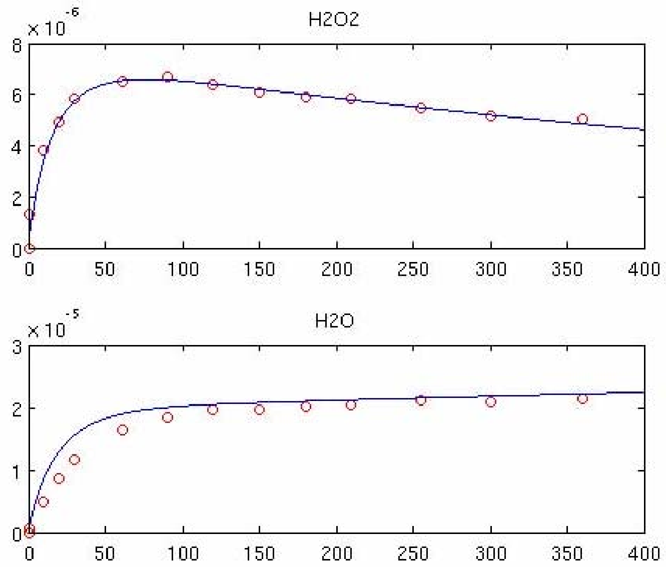


Fig. 1. Production of hydrogen peroxide and water (o) and fitting (-) at-5°C and 15 bar, partial pressure of H_2 1 bar and O_2 6 bar.

References

[1]. Voloshin, Y.; Halder, R.; Lawal, A. Kinetics of hydrogen peroxide synthesis by direct combination of H_2 and O_2 in a microreactor. Catalysis Today 2007, 125, 40.

[2]. Melada, S.; Rioda, R.; Menegazzo, F.; Pinna, F.; Strukul, G. Direct synthesis of hydrogen peroxide on zirconia-supported catalysts under mild conditions. Journal of Catalysis 2006, 239, 422.

[3]. Inoue, T.: Schmidt, M. A.; Jensen, K. F. Microfabricated multiphase reactors for the direct synthesis of hydrogen peroxide from hydrogen and oxygen. Industrial and Engineering Chemistry Research 2007, 46, 1153.

Acknowledgements

Pierdomenico Biasi gratefully acknowledges the PCC (process chemistry centre), Abo Akademi, Finland and the Johan Gadolinian scholarship for financial support.

DYNAMICS OF FIRST-ORDER PHASE TRANSITIONS

Bykov V.I.[1], Tsybenova S.B.[2]

[1] *Mendeleev University of Chemical Technology, Moscow, Russia, vibykov@mail.ru*
[2] *Moscow Humanitarian Pedagogical Institute, Moscow, Russia, tsybenova@mail.ru*

It is well known that first-order phase transitions are frequently associated with noticeable heat effects. For example, melting is characterized as an exothermal process, whereas liquid–solid transformation can occur with heat evolution. In the simplest case, the rates of these transitions can be described as a function of temperature in a standard way using the classical Arrhenius relationship. The nonlinearity and sluggishness of thermal processes in the small vicinity of phase transitions can give rise to typical nonlinear and non-steady-state effects, namely, the multiplicity of steady states and oscillations [1–7].

Here, we propose the simplest dynamic model of a phase transition and perform its parametric analysis. Conditions have been recognized for the existence of three and five steady states; the ranges of the parameters where auto-oscillations exist in a dynamic system have been found; and characteristic parametric and phase portraits of the mathematical model have been designed. The process dynamics in the vicinity of a phase-transition point has been shown to be rather complex. The processes observed here include the hysteresis of temperature dependences, undamped concentration and temperature oscillations, and considerable dynamic bursts during the establishment of a steady state.

For phase transitions of the type

$$\rightleftarrows F_2 \qquad (1)$$

in a system where there is heat exchange with the environment, a dimensionless spatially homogeneous model in accordance with [4] can be represented as

$$= -f_1(y)x_1 + f_2(y)(1 - x_1), \qquad (2)$$

$$= \beta_1 f_1(y)x_1 + \beta_2 f_2(y)(1 - x_1) + s(1 - y), \qquad (3)$$

where

$$(y) = Da_i \exp\left(\gamma_i\left(1 - \frac{1}{y}\right)\right), \qquad = 1, 2, \qquad (4)$$

x_1 and y are dimensionless concentration and temperature, respectively; dimensionless parameters Da_i, γ_i, and β_i according to Frank-Kamenetskii, respectively, characterize the rates, activation energies, and heats of $F_1 \rightarrow F_2$ and $F_2 \rightarrow F_1$ phase transitions; and s is a parameter characterizing the heat-exchange intensity with the environment.

Mathematical model (2) + (3) is a set of two differential equations with characteristic nonlinearities (4). In combustion theory and theoretical foundations of chemical reactors, such a model is a conventional subject of parametric analysis [5–12]. Model (2) + (3) is specific in that it refers a non-flow-through system and contains two exponents (4), considerably supplementing the variety of the dynamic and nonlinear properties of the system as shown in our earlier investigations. Here, we report the parametric analysis of dynamic system (2) + (3), including analysis of the number and steadiness of steady states, the construction of parametric dependences of steady-state characteristics, design of parametric and phase portraits, and calculations of temporal dependences characterized by dynamic bursts and undamped concentration and temperature oscillations.

To summarize, dynamic model (2) + (3) can be regarded as the simplest basic model of a first-order phase transition. The parametric analysis of this model shows that it can have one, three, or five steady states. The parameter regions have been found where auto-oscillations exist in a dynamic system; characteristic parameter and phase portraits have been designed for the mathematical model. The process dynamics in the vicinity of a phase transition point can be rather complex. Its characteristic features can be hysteresis of temperature dependences, undamped temperature and concentration oscillations, and considerable dynamic bursts as the system tends to acquire a steady state.

References

[1]. Bykov, V.I. and Tsybenova, S.B., *Gorenie Plazmokhim.*, 2007, vol. 5, no. 1/2, pp. 120–155.

[2]. Bykov, V.I. and Tsybenova, S.B., *Dokl. Phys. Chem.*, 2000, vol. 374, nos. 4–6, pp. 196–199 [*Dokl. Akad. Nauk*, 2000, vol. 374, no. 5, pp. 640–643].

[3]. Bykov, V.I. and Tsybenova, S.B., *Fiz. Goreniya Vzryva*, 2001, vol. 37, no. 5, pp. 36–48.

[4]. Bykov, V.I. and Tsybenova, S.B., *Teor. Osn. Khim. Technol.*, 2003, vol. 37, no. 1, pp. 64–75.

[5]. Bykov, V.I., Tsybenova, S.B., and Slin'ko, M.G., *Dokl. Phys. Chem.*, 2001, vol. 378, nos. 1–3, pp. 134–137 [*Dokl. Akad. Nauk*, 2001, vol. 378, no. 2, pp. 214–217].

[6]. Bykov, V.I., Tsybenova, S.B., and Slin'ko, M.G., *Dokl. Phys. Chem.*, 2001, vol. 378, nos. 1–3, pp. 138–141 [*Dokl. Akad. Nauk*, 2001, vol. 378, no. 3, pp. 355–358].

[7]. Bykov, V.I., *Modelirovanie kriticheskikh yavlenii v khimicheskoi kinetike* (Modeling of Critical Phenomena in Chemical Kinetics), Moscow: Editorial URSS, 2007.

Acknowledgements

This work was supported by the Federal Agency of Education of the Russian Federation in the frame of the Targeted Analytical Program “Development of the Scientific Potential of Higher Education Institutions for 2009–2010” (project no. 2.1.1/2104).

ELECTROCHEMICAL OXIDATION OF AQUEOUS SOLUTIONS CONTAINING UREA ON ACTIVE OR NO-ACTIVE ANODES

Cataldo M., **Fino D.***, **Spinelli P.**

Department of Materials Science and Chemical Engineering,
Politecnico di Torino,
Corso Duca degli Abruzzi 24, 10129, Torino, Italy
*Tel./Fax 011.564.4710/4710; *corresponding author: debora.fino@polito.it*

Electrochemical reactors are used for wide range of applications from analytical determinations to full-scale synthesis and environmental treatments[1].

The present work describes the anodic decomposition of urea using Pt and SnO_2-Sb_2O_5/Ti anodes for regenerative treatments of wastewater of varying urea concentrations as a consequence of some industrial synthesis. The SnO_2-Sb_2O_5/Ti anodes have been prepared by several techniques in our laboratories and they were fully characterized. Cyclic voltammetries (CV) and tests in electrochemical cell have been carried out in an aqueous solution containing urea. Numerous experiments have been analyzed to evaluate the optimal operating conditions that permit higher reaction kinetics as a function of current density, temperature, urea and electrolyte concentrations to be obtained. The electrochemical oxidation experiments have been carried out in a batch recirculation reactor, whose important features are a great flexibility and easy mode of operation. This reactor has been equipped with an anodic compartment and a cathodic one, divided by a cationic membrane (CMX Neosepta-Tokuyama Soda Co. Japan) than enables the transfer of NH_4^+ produced as a consequence of the urea oxidation reaction [2]. This aspect depends on the chemical nature of the electro-oxidized compounds. The solution in the anodic and cathodic compartments have periodically been sampled by means of a spectrophotometer (Cary 5000 Varian) and a colorimeter (model 975-MP Orbeco-Hellige) to determine, during the treatment, all the dissolved chemical species. The important parameters, such as ORP, pH, and conductivity, which are useful for investigating the electrochemical process, have continuously been measured (ION 450 Hach-Lange). Furthermore different cyclic voltammetries were studied in a 400 mL cell connected to a Voltalab (PGZ301 Radiometer) potensiostat, using Pt as the counter-electrode, Hg/Hg_2SO_4 as the reference electrode, alternatively Pt or SnO_2-Sb_2O_5/Ti as the working electrode immersed in a 1 M N $NaClO_4$ solution. Fig. 1 shows the first CV cycle with and without urea, and significant differences can be observed between the two curves.

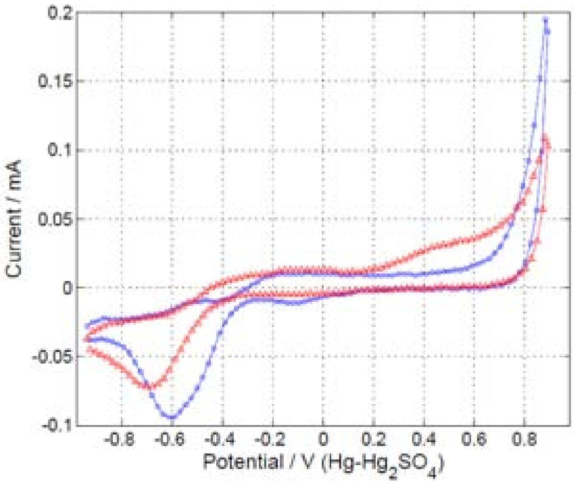


Figure 1. Cyclic voltammetry at 10 mV s^{-1} of the Pt/Ti anode without urea (blue curve) and with urea (0.1 M) plus electrolyte (1 M NaClO$_4$) (red curve). Reference electrode: Hg/Hg$_2$SO$_4$

In all cases, the CVs in the presence of urea show an adsorption peak between -0.5 V and -0.25 V, immediately followed by a peak attributable to the formation of platinum higher-oxides (PtO$_{x+1}$) from platinum oxide (PtO$_x$). This latter feature is evident for both curves in the potential range from -0.25 V to 0.12 V, whereas an ill-defined peak generated by urea oxidation is displayed in the red curve, at higher potentials,. During oxygen evolution, it can be noted that, in the urea CVs, there is a decrease of the current density with respect to those recorded in the CVs without urea, probably due to a strong adsorption of the organic molecule on the anode surface. This latter point finds a substantial confirmation, in the displacement of the PtO$_{x+1}$ reduction peak at the lower potential, observed in the CVs with urea; furthermore, the reduction current of the platinum higher-oxides, in the presence of organic substance, is lower than that measured without the contaminant. More cycles of the same test have been carried out, and these have pointed out a perfect overlapping of the voltammetric profile obtained in the presence of urea, suggesting that the overall adsorption/desorption processes are reversible [3]. The change of urea concentration with time was determined by means of UV analysis and have already shown a strong abatement in the first hour of treatment. Possible reaction paths have been considered to envisage the nature of the intermediate oxidation products, which are always present in advanced oxidation processes.

References

[1]. Trinidad P., Walsh F., Int. J. Engeng **(1998)** 14, 431-441.
[2]. Jara C., Fino D., Spinelli P., J. Appl. Electrochem. **(2008)** 38, 915-922.
[3]. Climent V., Rodes A., Orts J.M., Aldaz A., Feliu J.M., J. Electroanal. Chem. **(1999)** 461, 65-75.

CHEMPAK SOFTWARE PACKAGE: OPTIMIZATION OF THE CHEMICAL REACTION KINETICS WITH USING OF COMPUTER SIMULATION

Chernykh I.G.

Institute of Computational Mathematics and Mathematical Geophysics SB RAS, Novosibirsk, Russia

At present, mathematical modeling is successfully used to support decision making in the development and modernization of chemical processes and reactors. Note that modernization of chemical processes and reactors is the interdisciplinary problem, which requires the involvement of experts in physics, chemistry and mathematical modeling. Determination of kinetic scheme of chemical reactions is a key stage in devising a mathematical model of reactor. Such a scheme includes the proposed reaction mechanism and the values of rate constants for individual reaction steps. It was shown elsewhere that different kinetic schemes used to describe a certain reactive flow with the same gas-dynamic parameters lead to radically different simulation results. In the literature, a process can be described by alternative schemes due to the prevalence of semiempirical models of chemical kinetics, with stoichiometric equations being used instead of elementary steps. Although semiempirical representations are of limited use, the development of such kinetic schemes is quite topical, as they provide a model of reactive medium, which is adequate in a specified range of conditions. The development of semiempirical models and determination of rate constants for individual reaction steps are based on the full-scale and computational experiments. The computational experiment aimed at determination of kinetic scheme is the iterative process including the following stages: advancement of a postulated reaction scheme; generation and solution of a stiff nonlinear set of ordinary differential equations that describes chemical transformations of substances within the proposed scheme; and comparison of numerical and experimental data on the reaction kinetics.

In this paper CHEMPAK software package presented. CHEMPAK package makes possible to generate a set of ordinary differential equations corresponding to the scheme of chemical reactions. This set with relevant kinetic and heat parameters is automatically included in the model computations. The main features of CHEMPAK software package are an easy-to-use interface adapted for modification and evaluation of kinetic scheme of a chemical process, an automatic solver of chemical kinetic tasks, a network chemical database for storage of chemical reaction systems and other chemical data, the possibility of using the reactor models with chemical reaction models. There are some software plugins included in CHEMPAK. These plugins gives possibility of preparing and using data to/from FLUENT and CHEMKIN. The CHEMPAK architecture is shown schematically in Figure 1. CHEMPAK can be used for different purposes such as an optimization of kinetics of sugar synthesis or optimization of homogeneous pyrolysis of C_2-C_3 hydrocarbons. Computer simulation of kinetics of homogeneous pyrolysis of C_2-C_3 hydrocarbons was used in FLUENT for complex task of CFD modeling with chemical reactions. More detailed description of usage of CHEMPAK is in [1-5].

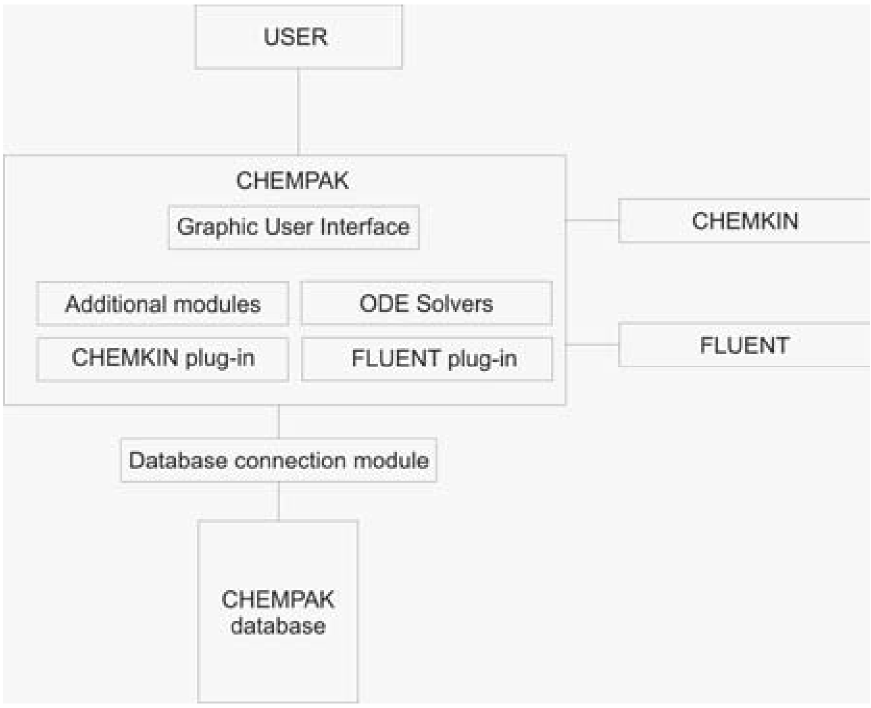


Figure 1. CHEMPAK architecture scheme.

The content presented in this paper was partially supported by the Russian Foundation for Basic Research (grant No. 08-01-00615); SB RAS integration programs No. 40.

References

[1]. Chernykh I.G., Zasypkina O.A. Computer simulation of the sugar synthesis of Butlerov reaction in a circumstellar disk. II International Conference "Biosphere Origin and Evolution", Abstracts, Greece, **2007**, p.187.

[2]. Chernykh I.G., Stoyanovskaya O.P. Homogenous pyrolysis of C2-C3 hydrocarbons under CO2-laser-induced heating. 4th EFCATS School on Catalysis ‘Catalyst Design - from Molecular to Industrial Level’, Russia, **2006**, p.165.

[3]. Chernykh, O. Stoyanovskaya, and O. Zasypkina. ChemPAK Software Package as an Environment for Kinetics Scheme Evaluation. // Chemical Product and Process Modeling. **2009**. Vol. 4, Iss. 4, Article 3, pp.1-15.

[4]. I.G. Chernykh, T.I. Mischenko, V.N. Snytnikov and Vl.N. Snytnikov. Computer Simulation Of Chemical Processes And Fluid Flows In Chemical Reactors // Proc. of The Second Int. Symp. on Comp. Mech. (ISCM II) in conjunction with The Twelfth Int. Conf. on the Enhancement and Promotion of Comp. Methods in Engineering and Science (EPMESC XII). - Honk Kong and Macao, **2009**.

[5]. I.G. Chernykh, T.I. Mischenko, V.N. Snytnikov, Vl.N. Snytnikov. Modelling fluid flow and het transfer in chemical reactor with using laser energy for heating the reactants // Proc. 7th World Conf. on Exp. Heat Transfer, Fluid Mech., Thermodyn. Krakow, **2009**, pp. 1683-1688.

Acknowledgements

The content presented in this paper was partially supported by the Russian Foundation for Basic Research (grant No. 08-01-00615); SB RAS integration programs No. 40, 26.

COMPUTER SIMULATION OF ENDOTHERMIC PROCESSES IN FLOWING REACTORS USING RADIATION ENERGY

Chernykh I.G.[1], **Mischenko T.I.**[2], **Snytnikov Vl.N.**[2], **Snytnikov V.N.**[2]

[1]*Institute of Computational Mathematics and Mathematical Geophysics SB RAS,*
pr. Ak. Lavrentieva, 6, Novosibirsk, 630090, Russia, chernykh@ssd.sscc.ru
[2]*Boreskov Institute of Catalysis SB RAS, pr. Ak. Lavrentieva, 5, Novosibirsk, 630090,*
Russia, snyt@catalysis.ru

A flow reactor with the reactants heated by continuous CO_2 laser radiation is proposed for studying the gas phase homogeneous reactions. Ethane pyrolysis yielding ethylene is considered as an example of such chemical process. For this process, a mode of 'energetic catalysis' is feasible, where increasing energy absorption in the volume is related with the increased content of target product. The mode of 'energetic catalysis' was implemented at transformation of laser energy into thermal power using the sensitization properties of ethylene. Three-dimensional calculation of the gas-dynamic reactants flows and their mixing was made with the FLUENT software package showed the presence of the modes where reaction zone with a high content of C_2 hydrocarbons is localized in the center of reactor, which was confirmed by experiments.

For the researches of the gas phase homogeneous reactions there was produced new chemical reactors – cruciform quartz flowing reactor [1] and multiinput cylindrical flowing reactor [2]. Ethane-ethylene gas mixture flow is perpendicular to the laser beam in case of reactor from [1] and parallel in case of reactor from [2]. All of these reactors have been included to the experimental setup [2] with CO_2 laser unit. Ethane-ethylene mixture consists from the ~32% of ethylene and ~68% of ethane. The main idea of new chemical reactors based on formation of compact reaction zone in the center of chemical reactors with blocking of reaction zone from the optical windows by the inertial gases (Ar for example). More detailed description of the experiments is in [2]. Detailed distribution of hydrocarbons was received by the chromatographic analysis. Ethane conversion increased up to 75% with laser power between 32 and 60 W/cm^2. Maximum ethylene output was 37% with laser power 40 W/cm^2 that conformed 51% of ethane conversion. Experimentally founded that the concentration of ethylene between 4 and 6 %vol. is insufficient for the ethane conversion starting. The reaction zone was accepted with ethylene values higher than 6%vol. That was one of the main criteria for the forming of reaction zone during computer simulation. Another main criterion was the isolation of ethane-ethylene mixture from the reactors walls and optical windows.

The main feature of the computer simulation of these processes is a complex problem of CFD modeling with chemical reactions modeling and laser energy consumption of ethylene in gas mixture factor. Chemical reactions are flowing in growth of laser energy absorption conditions and with the growth of ethylene content in gas mixture. Special software module was written for the FLUENT mathematical model adaption for these conditions.

Results of computer simulation of processes in reactor [2] are closed to the experiments. Compared results of the computer simulation and experimental results are received for the room temperature conditions. The hydrocarbons mass fraction near the walls was 15% which corresponds to 5% ethylene mass fraction in ethane-ethylene gas mixture. The hydrocarbons mass fraction at the center of the reaction zone was up to 60%vol. at the same time.

There are some differences in gas flows between room temperature conditions and a laser energy absorption condition has been showed for the reactor [1]. Mass fraction of the ethylene near the optical windows was ~3% and at the center of reaction zone was 20% at the room temperature conditions. Mass fraction of the ethylene from the optical windows to the border of reaction zone was ~2%vol. and at the center of reaction zone was 15-20% in case of laser energy absorption scheme.

Gas flows in room temperature conditions and with laser energy absorption by ethylene in chemical reactors has been showed. The possibility of compact reaction zone generation for the endothermic processes in flowing reactors with isolation of walls and optical windows from the pollution by reactants has been described.

References

[1]. [V.N. Snytnikov, T.I. Mischenko, Vl.N. Snytnikov, I.G. Chernykh. Physical and chemical processes in flowing reactors using radiation energy (in print).

[2]. V.N. Snytnikov, T.I. Mischenko, Vl.N. Snytnikov, I.G. Chernykh. A reactor for the study of homogeneous processes using laser radiation energy.// Chemical Engineering Journal. **2009**. 150. pp. 231-236.

[3]. FLUENT. http://www.fluent.com

Acknowledgements

The content presented in this paper was partially supported by the Russian Foundation for Basic Research (grant No. 08-01-00615); SB RAS integration programs No. 40, 26.

MODELLING KINETICS OF PROCESS LIQUID-PHASE EPOXIDATION OF PROPYLENE IN MEDIUM OF ISOPROPANOL

Danov S.M., **Sulimov A.V.**, **Ovcharov A.A.**, **Ryabova T.A.**

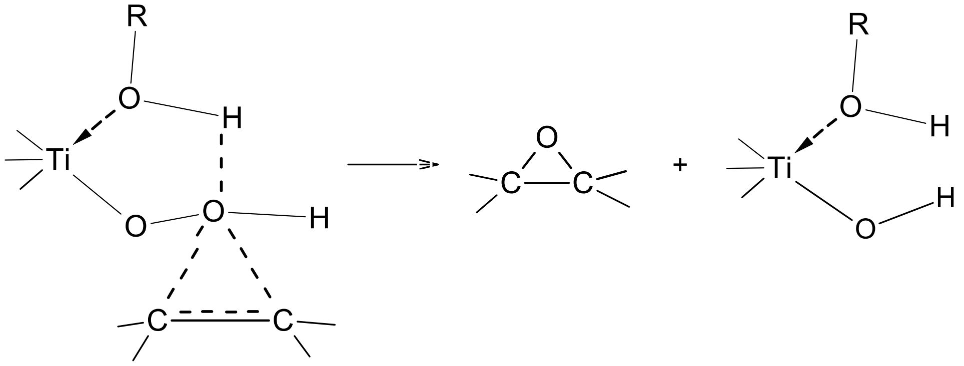
Dzerzhinsk Polytechnic Institute (branch) R.Y. Alekseev Nizhny Novgorod State Technical University, Dzerzhinsk, Russia, asulimov@mail.ru

Propylene oxide is one of the most important products of basic organic synthesis. Having high reactivity, it easily reacts with compounds of different classes that allows to get a considerable quantity of products on its basis (polyurethanes, glycols, polypropylene oxide rubbers, nonionic surfactants, cosmetics, medicines, etc.).

Currently, according to the majority of researchers, method of direct liquid-phase epoxidation of propylene by aqueous solution of hydrogen peroxide in the medium of organic solvent in the presence of the heterogeneous catalyst is the most promising. The distinctive feature of the process is that it carries out at moderate temperatures (30-60 °C), low pressures (6-8 atm.) and it's attractive for environmental aspect as water is the main by-product resulting the process.

Our studies have shown that methanol is more effective for use as the solvent of this process because there are observed the highest yield of propylene oxide. However, in view of high cost of hydrogen peroxide it is considerable to use isopropanol as a solvent that allows to join technologies of reception hydrogen peroxide and reception oxide propylene. Such integration gives the possibility to create a balanced process where the isopropanol acts as a reagent in the first stage, and as a solvent on the second one, that finally results to decreasing the cost of propylene oxide. Therefore, the purpose of this study was generation of the kinetic equation describing the process of epoxidation of propylene by aqueous solution of hydrogen peroxide in the medium of isopropyl alcohol in the presence of titanium-containing zeolite in the conditions of the periodic reactor.

In accordance with exist conceptions, during the process of the synthesis of propylene oxide there is formation of a transitional complex with an active oxygen atom that can be transmitted to propylene. Generalized process can be illustrated by the following scheme:



Besides, it was experimentally confirmed that the formed propylene oxide inhibits the epoxidation process. Apparently, this is due to the fact that propylene oxide also adsorbs on the active centers of the catalyst, thereby reducing the proportion of the free surface and the possibility of formation of five-membered complex. Therefore the concentration of propylene oxide should be considered in the kinetic equation.

Thus, in the process of epoxidation can be nominally detailed the following stages: adsorption of hydrogen peroxide, the superficial reaction and desorption of propylene oxide. And each of these stages can be limiting. Studying the influence of various factors on the process, we have established that there is observed increase of epoxidation process rate at increas concentrations of propylene and hydrogen peroxide. Based on it we can conclude that the adsorption stage of hydrogen peroxide is not limiting

To receive the kinetic model we have made the assumptions that the rate-limiting step of the process of liquid-phase epoxidation of propylene by hydrogen peroxide at heterogeneous catalysts is the superficial reaction, at that all of the adsorbed components are in equilibrium; reaction takes place between hydrogen peroxide adsorbed on the surface of the catalyst and propylene located in the dissolved state. According to these assumptions we have received the following kinetic model:

$$r = \frac{k_1 \cdot K_{H_2O_2} \cdot [H_2O_2] \cdot [C_3H_6]}{1 + K_{H_2O_2} \cdot [H_2O_2] + K_{C_3H_6O} \cdot [C_3H_6O]}$$

The experimental data were processed by the method of nonlinear LS (least squares). As the result, we calculated the values of parametres of the kinetic equation providing an adequate description of all experiments that were carryed out.

THE INVESTIGATION OF REACTIONS AROMATIC ISOCYANATES WITH OPEN-CHAIN ANALOGUES OF CROWN ETHERS

Davletbaeva I.M., **Gumerov A.M.**, **Ahmetshina A.I.**

Kazan State Technological University, 420015, K. Marks Str., 68
davletbaeva09@mail.ru

In last decade there are vast investigations in polymer science directed to producing of polymer materials with special properties. One of the approaches to create such kind of materials based on including of molecular objects which are able to donor-acceptor interaction into their structure.

The interest to investigation of characteristics of molecular organization of polymers based on open-chain analogues of crown ethers and aromatic isocyanates is caused by the possibility of getting polymers with predictable electro-physical characteristics.

The purpose of this work is investigation of reaction conditions stimulating to O-polyisocyanate groups formation and stabilization and the influence of intermolecular interactions at photoluminescent activity and electro-physical characteristics of polymers.

As an assumption during modeling it was accepted that polymerization rate doesn't depend on polymer chain length. Model parameters: initiation, polymerization, cyclization and urethane groups' formation rate constants. Kinetic equations describe time-changing concentration of components.

It was established that cyclization and polymerization rate constants ratio can be accepted as a possibility criterion of opening of isocyanate groups on N=C- or C=O part. Polymerization rate constant corresponds to polyconnection caused by carbonyl opening of isocyanate groups.

Supramolecular structures formatting in the presence of terminal O-polyisocyanate chain can have an effect on spectral domain of photoluminescence and reducing of bulk electrical resistivity.

PP-I-15

THE MECHANISM OF SELF-OSCILLATIONS GENERATION IN CSTR. CONSECUTIVE REACTION

Deyun E.V., Andrianova Z.S., Kustova L.V., Samoilenko N.G., Korsunskiy B.L.

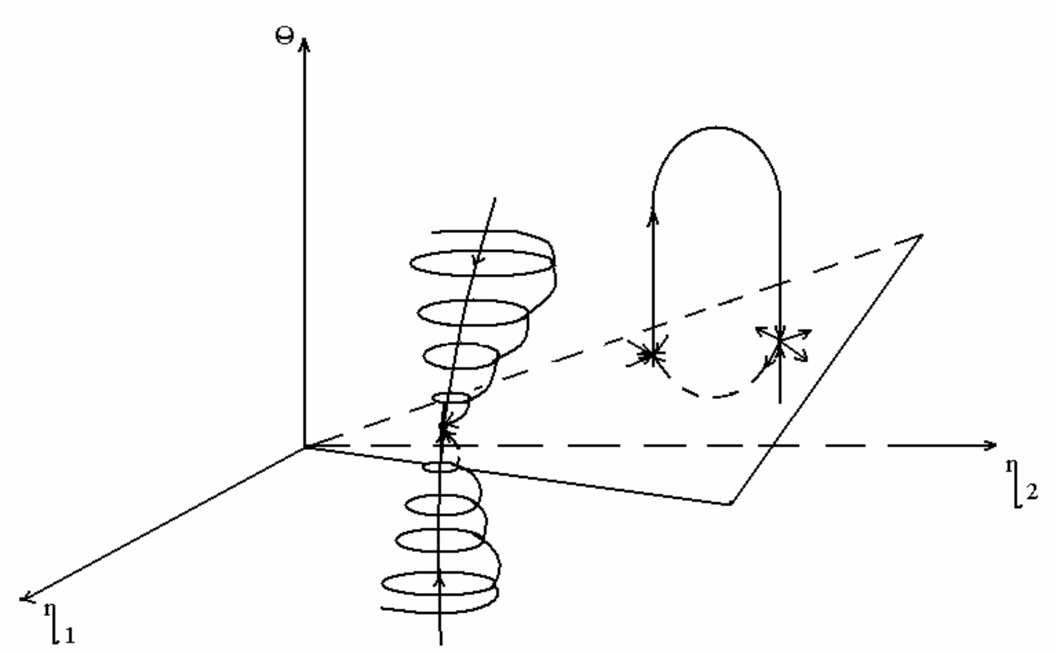
Institute of Problems of Chemical Physics of the Russian Academy of Sciences.
Academician Semenov avenue, 1, 142421 Moscow region, Chernogolovka, Russia.
E-mail: kors36@mail.ru

The mechanism of self-oscillation generation and damping in CSTR with two consecutive exothermal first order reactions has been studied. It has been shown, that in the system with only one steady state oscillations arise “softly” on the lower border of self-oscillatory modes (small values of Semenov parameter) but on the upper border (great values of Semenov parameter) oscillations damp "rigidly", i.e. the stable limiting cycle merges with an unstable one.

For adiabatic reactor the impossibility of existence of the closed trajectories in phase space has been proved.

In contrast to autocatalytic and concurrent reactions, in the case of consecutive reactions the occurrence not only of one and three, but also of five steady states is probable. The area of five steady states arises inside of the area of three steady states. When the relationship between activation energies of separate stages is changed the part oh this area penetrates through the upper border turning into an additional subarea of three steady states.

The mechanism of self-oscillations generation for the cases of three and five steady states has been investigated. For the purpose in parametrical space Se - Da (Se – Semenov criterion, Da – Damköhler criterion) the areas of steady states multiplicity have been calculated. The analysis of steady states transformation and self-oscillations generation inside multiplicity areas has allowed proposing the mechanism of a "rigid" birth of a stable limiting cycle (a mathematical image of self-oscillations). This mechanism is founded on the formation of saddles-knots trajectories loop.



The qualitative picture of stable limiting cycle formation for the system with three steady states is presented on the figure.

PP-I-16

DEVELOPMENT OF MODELING SYSTEM FOR CALCULATION OF STAGES OF LINEAR ALKYLBENZENES PRODUCING BASED ON RECYCLING RAW

Dolganov I.M., **Kirgina M.V.**, **Ivashkina E.N.**

Tomsk Polytechnic University,
Lenin av. 30, Tomsk, Russia, 8(3822)563443, dolganovim@sibmail.com

Currently, the world has substantially increased the need for various detergents, so production of the main component of synthetic detergents (SD) – alkylbenzosulphonate and linear alkyl benzene (LAB and LABS) will grow also. Alkylbenzosulphonate are anionic surfactants and have good cleaning ability, allowing them to hold the leading position among other detergents. Thus, there is an obvious need to increase the production of LAB [1].

The aim of work is the creation of a unified computer system simulating various options for reconstruction of chemical-technological systems, including closed ones, containing recycling materials.

Complex for LAB and LABS production includes three technology-related reactor units: dehydrogenation of n-paraffins, dehydration of hydrogenation process by-products – diolefines - to monoolefines, and alkylation. In the process of dehydrogenation of a relatively low conversion of n-paraffins – 12-13% (in fact 10%) is adopted by the project, so the alkylation unit receives a significant amount of normal paraffins, which, after alkylation are returned as recirculation to dehydrogenation unit. But other options for recycling of unreacted paraffins (after dehydrogenation reactor, after the hydrogenation reactor) are also possible [2].

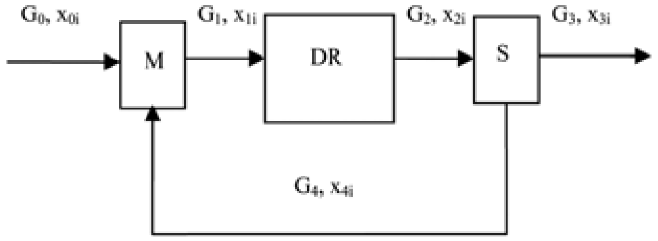


Fig. 1. Scheme of dehydrogenation process with recycle of unreacted paraffins: M – mixer; DR – dehydrogenation reactor; S – separator

Mathematical model of recirculation:

$$x_{1i} = (1-\varphi)\cdot x_{0i} + \varphi\cdot x_{4i}; \quad x_{3i} = (x_{2i} - \varphi\cdot x_{4i})/(1-\varphi); \qquad \varphi = \frac{G_4}{G_2} = \frac{G_4}{G_1}, \varphi = 0..1; \qquad (1)$$

Here G_n – total mass flow, x_{ni} – mass fraction, %, n – flow number, n = 0...4; i – component number, i =1...N, N – number of components in the flow.

Thus, knowing the composition of raw materials (x_{0i}), composition of the waste stream (x_{4i}), and mass ratio of recycling (φ), we can calculate the composition of the raw materials entering the reactors of dehydrogenation (x_{1i}) and hydrogenation (x_{3i}).

The calculation results are shown in fig. 2.

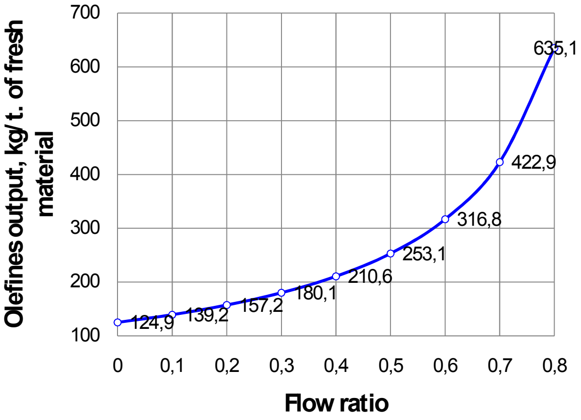


Fig. 2 - Dependence of olefins yield per ton of fresh material on the ratio of flows

The presented dependence shows that the recycling ratio equal to 0.3 is the best, as an increase in the yield of olefins is 55.2 kg per ton of fresh material (44%), while an increase in diolefines output is 1,8 kg per ton of fresh raw material (72%).

The model developed and programs created on its basis would be applied as simulators and expert systems for engineering and technical personnel of the plant.

The software product allows to calculate the characteristics of the current process, which can not be identified by laboratory testing or on the current instrument readings. Also, using the simulation program can predict the results of changes in technological regime and reconstruction of the existing installation.

Total revenue from the introduction of simulation program will be about 225 thousand rubles per day. As results of researches certificates of state registration of computer programs were received.

References:

[1]. Kravysov A.V., Ivashkina E.N., Yuriev E.M., Ivanchina E.D. IT-technologies in problems of the industrial process of higher paraffins dehydrogenation solving; Tomsk Polytechnic University - Tomsk: STT, 2008. – 230 p.

[2]. Bannov P. G. Processes of oil refining. - M.: TsNIITEneftehim, 2001. - 625 pp.

PP-I-17

PHOTOVOLTAIC SOLAR POWERED ELECTROCHEMICAL OXIDATION (PSEO): KINETICS OF THE REMOVAL OF TOTAL ORGANIC CARBON FROM LIGNOSULPHONATE WASTE-WATER

Dominguez-Ramos A., Aldaco R., Irabien A.

Department of Chemical Engineering and Inorganic Chemistry, University of Cantabria, Avda. Los Castros s/n 39005, Spain, domingueza@unican.es

The release limits of pollutants to water bodies are becoming more and more stringent as covered in the BREF documents regarding Best Available Technologies (BATs) for waste-water treatment in the European Union [1]. Electrochemical oxidation using boron doped diamond electrodes could fulfill the technical requirements to remove any kind of organic dissolved species in liquid effluents [2], but nowadyas more R&D (and later innovation) is requested for future implementation. The limitations are due to two different issues: the current cost per electrode unit area and the high specific energy consumption per unit of volume treated [3]. The energy cunsumption is a serious handicap due to the additional environmental loads due to the electrical consumption to generate the requested current density between electrodes. To prevent these environmental loads, a novel process called Photovoltaic Solar powered Electrochemical Oxidation was developed, in which the energy collected from a set of photovoltaic modules is directly inyected into an electrochemical reactor [4].

Consequently, the kinetic rate *r* is based on the instanteneous solar irradiation *g*. Based on previous experimental results obtained at galvanostatic conditions using a power supply, a kinetic rate expression was proposed as a function of the applied current density *i*. A linear relationship between *g* and *i* was proposed to relate both variables, so finally it leads to Eq. 1:

$$-r = \frac{k_1 i(g)}{1 + k_2 i(g)} C \qquad \text{Eq. 1}$$

Where k_1 and k_2 are parameters that integer photovoltaic module characteristics and the kinetic values obtained under current controlled conditions; C represents the Total Organic Carbon concentration. From Eq. 1, it is seen that under high irradiation conditions, the process becomes mass-transfer controlled and a first order kinetic is oberved. Only under very low irradiation conditions, the process is controlled by current density. Preliminary results of the performance of a PSEO pilot scale plant will given and the validity of the proposed kinetic rate will checked under different real effluents from a waste-water treatment plant.

References

[1]. European Union, Reference Document on Best Available Techniques in Common Waste Water and Waste Gas Treatment / Management Systems in the Chemical Sector, **2007**

[2]. Dominguez-Ramos, A., Aldaco, R., Irabien, A., Ind. Eng. Chem. Res., **2008**, 47, 9848-9853

[3]. Cañizares, P., Díaz, M., Domínguez, J.A., García-Gómez, J., Rodrigo,M.A., Ind. Eng. Chem. Res., **2002**, 41, 4187-4194

[4]. Dominguez-Ramos, A., Aldaco, R., Irabien, A., J. Chem. Technol. Biotech., **2010**, *in press*

Acknowledgements

The authors gratefully acknowledge the financial support of the Ministry of Science and Technology of Spain through the project CTM2006-00317 and the project CENIT Sostaqua.

DEVELOPMENT OF NEW GENERATION OF CATALYSTS ON FIBER GLASS WOVEN SUPPORT FOR RAW STYRENE PURIFICATION FROM PHENYL-ACETILENE IMPURITIES BY SELECTIVE HYDROGENATION METHOD

Dorokhov V.G.*, Barelko V.V.*, Bykov L.A.*, Basimova R.A.,
Pavlov M.L.**, Askarova A.V.****

**Institute of Problems of Chemical Physics RAS, Chernogolovka, Russia*
***Salavatnefteorgsintez Public Corporation, Salavat, Russia*
E-mail: lbik@icp.ac.ru

The work was aimed at the analysis of efficiency of the developed by the authors new catalysts on fiber glass woven base in processes of purification of raw styrene from phenyl-acetylene by selective hydrogenation of the impurity.

It was found from the tests that such type catalysts activated by noble metals are new perspective materials in both technological realization of the process and its reactor design. The analysis of related publications and patents justified the novelty of the catalysts proposed for technology of purification of the styrene fraction.

The experiments were performed using the sample of raw styrene fraction taken from Salavatnefteorgsintez Public Corporation.

The composition of the sample of raw styrene fraction was the following:

ethylbenzene	37.108 %
styrene	59.505 %
phenylacetylene	0,0072 %

The starting mixture was hydrogenated in a pilot reactor with vibration stirring in conditions of mass loading of the catalyst in liquid medium of the hydrogenated fraction at 25°C and 1 atm pressure of hydrogen. The process was realized on specially prepared catalysts using silica glass woven supports (96% of SiO_2).

All the catalysts used in the experiments were not pre-activated by hydrogen prior to hydrogenation. The ratio of the mass of the loaded catalyst to the volume of hydrogenated medium was ~ 0,03.

The following catalysts were prepared and tested:

Sample 1: Pd on silica grid, Pd content was ~ 0.15 wt.% .

Sample 2. Pd on silica grid, Pd content was ~ 0.15 wt.%, and copper was added; Pd : Cu = 4.2 :1.

Sample 3. The platinated catalyst on on silica grid, Pt content was ~ 0.1 – 0.2 wt.%.

Hydrogenation kinetics was determined by measurements of hydrogen absorption rate and chromatographic analysis of samples taken in course of the process. Three samples of the reaction mixture were taken in each experiment. The 1st sample was taken when the maximal hydrogen absorption rate was attained. The 2nd sample was taken when the absorption rate became two times lower. The 3rd sample was taken when hydrogenation was finished.

The data obtained from the analysis of dynamics of hydrogenation and the data of chemical analysis of the samples taken in the three successive points in the kinetic curves of hydrogenation for each of the prepared catalyst samples are evidence of that all the catalytic materials are characterized high enough activity and selectivity even at low temperatures and atmospheric pressure: sample 1 – phenylacetylene is fully removed in ~ 30 minutes at minor diminution of styrene; sample 2 – phenylacetylene is fully removed at catalytic contact of the fraction for 60-70 minutes; sample 3 – phenylacetylene is almost fully removed even in 15-20 minutes at high selectivity with respect to the styrene component.

As a result of the experiments, model design of the reactor for purifying styrene fraction from acetylene impurities by selective hydrogenation has been developed and assembled. This model can be used when designing and producing such reactors for industrial application. The proposed model reactor is equipped with a screw- or turbine-type mixer located the axis of the reactor shell inside a cylindrical frame, a fiber glass catalyst stripe is reeled on the cylindrical frame, the mixer forms a flow circuit of reaction medium movement about a cylindrical catalytic cartridge to provide intense contact of all the phases of reacting components: the styrene fraction and hydrogen with the catalyst. Reactor efficiency was tested on model reactions of liquid hydrogenation.

- The research work showed that purification of raw styrene fraction on proposed fiber glass catalytic materials is technologically promising process;
- The catalyst samples provide high selectivity in full removal of phenylacetylene from the hydrogenated fractions without noticeable loss of styrene during technological time of contacting (from 15 minutes to 1 hour) in the reaction medium in mild conditions (25-30 °C, atmospheric pressure).
- The experimental results are evidence of that potential of the proposed class of catalysts on glass woven base has not been exhausted so far. Optimization search for such catalytic systems can be widened by varying structure and composition of a catalytic matrix that allows one to shorten times of contacting, i.e. reactor volume at given process selectivity.

PP-I-19

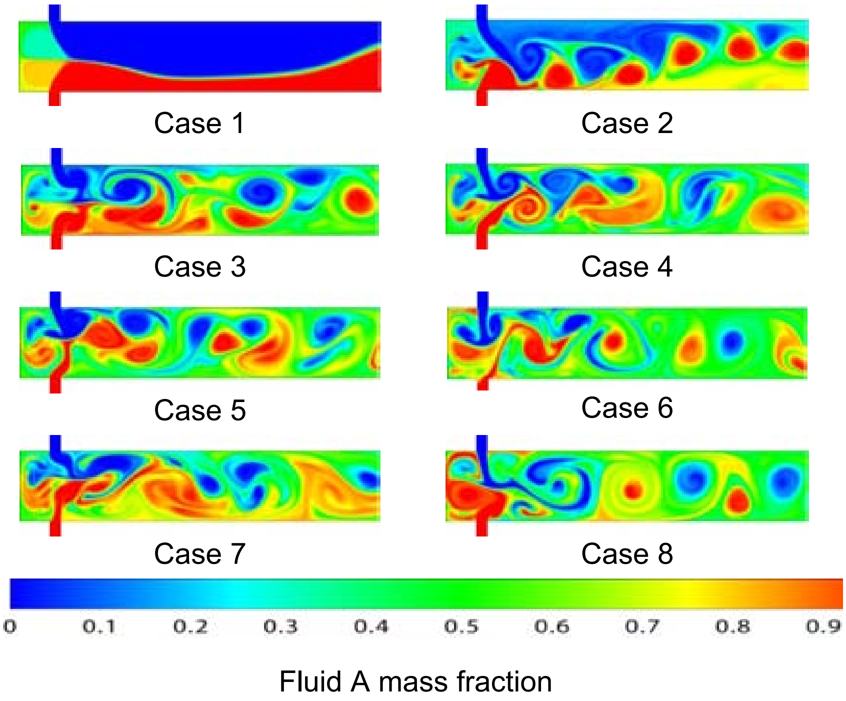
PROCESS INTENSIFICATION OF CIJR-A 2D TRACER SIMULATION STUDY

Ertugrul Erkoc[1], **Ricardo Jorge Santos**[2], **Paulo Jorge Gomes**[2], **Madalena Maria Dias**[2], **Jose Carlos Brito Lopes**[2]

[1]*TU Dresden, Institut für Verfahrenstechnik und Umwelttechnik, 01062 Dresden, Germany., ertugrul.erkoc@tu-dresden.de*
[2]*Laboratory of Separation and Reaction Engineering, Chemical Engineering Department, Faculdade de Engenharia da Universidade do Porto, Portugal*

Mixing is a critical step in many of the chemical processes where the degree of mixedness of the components controls the ensuing chemical reaction and as a result, the quality, and cost of the product. It is well known that the processes involving heat and mass transfer, mixing, drying ad combustion processes can be enhanced by turbulence[1]. Here the control of mixing is analysed in a geometry based on opposed jets, a Confined Impinging Jets Reactor (CIJR). Many impinging jet configurations have small dimensions, the jets have a diameter around 1mm, and because of that the jets are laminar likewise the flow regime inside the mixer, which presents a complex dynamic evolution above a low Reynolds number (Re) of 120: the flow regime is laminar chaotic for (Re>120) and laminar steady for Re<120. Previous study[2] showed that mixing in CIJR is very dependent on the operational parameters, for example momentum imbalance between the jets can compromise mixing, the reactions are slowed down and final product characteristics or distribution are affected. Furthermore a change in mixing conditions causes unused amount of reactants and undesired byproducts. Process Intensification (PI) of CIJR, by means of control of the operational parameters could result in reduction of secondary reactional steps and formation of by-products and can be the cornerstone for continuous processes applied to very fast chemical reactions with complex reactional schemes.

This work presents the study on the effect of the oscillation of the jets flow rate (active mixing) on the mixing dynamics of a CIJR at steady flow regime. To analyse the dynamics of mixing and the mixing efficiency, 2D CFD tracer simulations were performed for seven different active mixing strategies and compared against the case of unisdisturbed inlet feedstreams. Tracer concentration maps are shown in Fig.1 for the eight cases that were studied. The results showed that the mixing efficiency increases from 10% to 98% when using active mixing strategies. The parameters of the active mixing, amplitude and frequency of the jets flow rate oscillation also have an impact on the flow dynamics.


Case 1
Case 2
Case 3
Case 4
Case 5
Case 6
Case 7
Case 8

Ошибка! Текст указанного стиля в документе отсутствует.. 1. Fluid A mass fraction for different cases along with the un-pulsed case 1.

References

[1]. Wang, S.J. and A.S. Mujumdar, *Three-Dimensional Analysis of Flow and Mixing Characteristics of a Novel In-Line Opposing-Jet Mixer.* Industrial & Engineering Chemistry Research, **2007**. 46(2): p. 632-642.

[2]. Erkoç, E., et al., *Mixing dynamics control in RIM machines.* Chemical Engineering Science, **2007**. 62(18-20): p. 5276-5281.

Acknowledgements

Financial support for this work was in part provided by national research grants FCT/POCTI/EQU/345115/2000, PTDC/CTM/72595/2006 and by LSRE financing by FEDER/POCI/2010, for which the authors are thankful. Ertugrul Erkoc and Paulo Gomes acknowledges his Ph.D./scholarship by FCT, SFRH/BD/18901/2004 and SFRH/BD/24698/2005, respectively. Ricardo J. Santos acknowledges financial support from POCI/N010/2006.

PP-I-20

OPTIMIZATION OF THE ENGINEERING PARAMETERS FOR THE PRODUCTION OF ZEAXANTHIN IN A FLUIDIZED BED REACTOR

Eleazar M. Escamilla Silva[1], Mayanin Águilar Torres[2], Erika Ramos Ojeda[1]

[1] *Departamento de Ingeniería Química; Instituto Tecnológico de Celaya. Ave. Tecnológico y Antonio García Cubas S/N. Celaya Gto. C.P.38010. México*
eleazar.escamilla@itcelaya.edu.mx
[2] *Facultad de Química. Universidad Autónoma de Querétaro. Cerro de las Campanas S/N Col. Las Campanas. C.P. 76010. Querétaro, Qro, Manzanillo Colima, Mexico*

Abstract

The current trend in the food industry has taken up the use of natural products such as nutraceuticals, additives, flavourings and others. A special case is the use of pigments such as carotenoids, which are used for human and animal consumption. As is the Zeaxanthin, which is the main pigment of yellow corn and is used mainly as a pigment in the skin of poultry and egg yolk. The most appropriate process for the production of Zeaxanthin is by submerged fermentation using *Flavobacterium* sp.

The process for producing Zeaxanthin required determining the engineering parameters for design and scaling of industrial equipment, in this paper we pose the optimization of engineering parameters obtained correlated with dimensionless numbers such as are the Reynolds, Sherwood and Schmidt. The kinetics of the growth of *Flavobacterium sp*, was obtained by the application of Gompertz model with two parameters and showed a good correlation with our model: $\mathrm{Biomass}=ae^{-be^{-ct}}$ To determine the most important factors of the process we used an orthogonal experimental design. The factors analyzed were: Recycling, Aeration, pellet size and Carbon - Nitrogen. The variance analysis showed the most relevant factors: recirculation, aeration, Pellet size and finally the carbon – nitrogen respectively.

So through an unrestricted minimization is defined that the optimal production of Zeaxanthin during the experiment was 1.2506 mg/ml with an aeration of 1 vvm, carbon-nitrogen ratio of 1:1, recirculation rate of 40 ml/min and pellet diameter 3 mm. Achieving a correlation with experimental data determined by the Quasi-Newton numerical method. Well, was the best fit to the experimental data obtained during fermentation and In addition curves were developed describing the behaviour of the process, by means of dimensionless numbers. The proposed correlation for the Zeaxanthin production on basis to the engineering parameters obtained and the use of dimensionless numbers is given by Equation

$$\frac{Production}{Pellet\ mass\ (g)} = A\left(\frac{Dp * r * h}{\theta * v}\right)^{a} (Re)^{b} \left(\frac{Sh}{Sc}\right)^{c}$$

where r, h indicate the radius and height of the reactor, respectively, θ the reaction time, v the volumetric air flow rate A, a, b and c are the parameters obtained in the correlation. By STATISTIC software and application of simplex method were obtained the optimal parameters: A, a, b and c respectively.

Conclusions

We developed a methodology for the extraction and purification of Zeaxanthin from yellow corn with high yield and purity of 99.2%. The optimum concentration of zeaxanthin was 1.2506 mg/ml using the following composition in the culture medium: 13 g/l of dextrose, 5 g/l corn steep liquor, 20 g/l ammonium chloride, 5 g/l potassium hydrogen phosphate, 1.5 g/l magnesium sulfate heptahydrate, zinc sulfate heptahydrate, 0.05 M ferrous sulfate heptahydrate, cobalt chloride hexahydrate 0.05 M, manganese sulfate heptahydrate, 0.01 M and 4.5 g/l NaCl.The analysis of variance showed the importance of each of the variables analyzed in the experimental analysis. The most important was the recycle rate, then aeration rate, Pellet size and finally the carbon-nitrogen ratio. Of the 4 variables with 3 levels each, was obtained pellet size of 3mm, 1 vvm aeration, recirculation rate of 40 ml/min and a Carbon-Nitrogen ratio of 1:1. We developed a mathematical model using dimensionless numbers relating the variables involved in the process. This equation results in the production of Zeaxanthin obtaining a possible industrial scaling.

References

[1]. Britton G., Mendez H. D. **(1997).** Carotenoids and colour in fruit and vegetables. In *Phytochemistry of fruit and vegetables*. Tomas-Barberan TA and Robins RJ. Eds. Clarendon Press, Oxford. 11–27.

[2]. Christopher, D. B., Alvin, W. N. y Christopher, J. H. **(2002)** *Studies on the effect on mechanical agitation on the performance of brewing fermentation: fermentation rate, yeast physiology and development of flavor compound j.* Am. Soc. Brew. Chem 60(3): 101-106.

[3]. Mijts, B. N., Lee, P. C. y Schmidt-Dannert, C. **(2003).** *Engineering Carotenoid Biosynthetic Pathways.* Chem. Biol 10, 453.

[4]. Pasamontes, L., Hug, D., Tessier, M. y Hohmann, H.-P. **(1996)**. *Isolation and characterization of the carotenoid biosynthesis genes of Flaviobacterium sp.* Environ. Microbiol 185: 35-41.

[5]. Lotan, H., and F. Hirschberg, **(1995).** *Biosynthesis of carotenoides and their application*. Appl Sci. Publishers LTD. Great Britain, England.

[6]. Klein, J. y Wagner, F. **(1983)**. *Methods for the immobflization of microbial cells.* Appl. Biochem. Bioeng. 4, 11-51.

PP-I-21

SIMULATION OF DIRECTIONAL INTERMOLECULAR INTERACTIONS IN ORGANIC MONOLAYERS: TRIMESIC ACID ON SINGLE CRYSTAL (111) SURFACE

Fefelov V.F.[1], Gorbunov V.A.[1], Myshlyavtsev A.V.[1,2], Myshlyavtseva M.D.[1]

[1]Omsk state technical university, Omsk, Russia
[2]Institute of hydrocarbon processing SB RAS, Omsk, Russia
E-mail: Vitaly_Gorbunov@mail.ru

The production of self-assembled molecular films and supramolecular nanostructures of organic molecules on metalic surfaces is now the constantly growing field of researching [1,2]. The most of investigations are focussed on efforts to construct different organic-inorganic heterostructures with tailored properties such as reactivity, ultra-fast optical response and chemical sensing. Understanding the forces governing the arrangement of organic molecules is the key to controle and creation of self-assembled organic structures. A promising class of candidates to form supramolecular aggregates are moleculas with functional groups for hydrogen bond formation [1-3]. Hydrogen bonding can be used to tune the spatial arrangement of functionalized molecules on surfaces. The choice of molecular shape and size and especially the arrangement of hydrogen-bonding are crucial to the correct assembling of tailored supramolecular arrays [1-3].

The TMA molecule is carboxylic acid with threefold symmetry, comprised of a phenyl ring and three identical carboxyl end-groups in the same plane. TMA molecules at surface can form two stable hydrogen bonded structures at least [1,2,4] (Fig. 1b). The first structure unit is composed of sixfold rings of TMA with perfect arrangement of the hydrogen bonds in which each molecule is part of three neighbouring rings. Nextly, when we add molecules onto the surface, each sixfold ring accepts single TMA guest molecules in different positions until the saturated monolayer is reached – second stable hydrogen bonded structure.

In this study we propose the lattice gas model of self-assembled monolayer of TMA molecules on (111) surface. In the framework of the simplest model we consider that TMA molecule occupies only one site of two-dimensional triangular lattice. Each site of the lattice has its own occupation variable which equels to zero when site is empty; and 1 or 2 if the site occupied by TMA molecule with first or second plannar orientation, respectivly (see Fig. 1a). It is worth noting that the simplest case of our model is similar to the well-studied Blume – Capel model but our model is very anisotropic because interaction energy naturaly depends on relative location of neighbouring molecules.

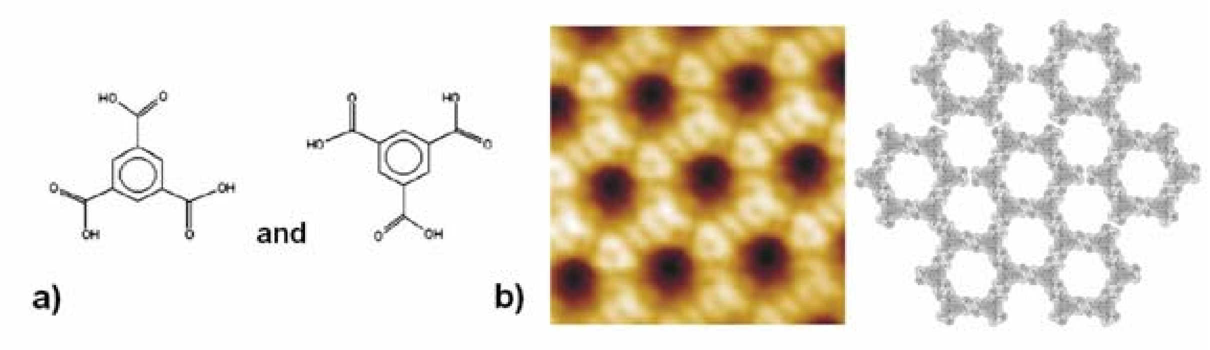


Fig. 1. a) Two possible orienatations of TMA molecule on (111) surface; b) STM and schematic image of structure composed of sixfold rings of TMA [2].

The model was studied with Monte Carlo and transfer-matrix techniques in grand cannonical ensemble. The analysis of calculating results allow us to mark out two limit cases of phase behaviour of the system: (1) The phase composed of sixfold rings of TMA is formed through the first-order phase transition from disordered lattice gas and, nextly, when we add molecules onto the surface, each sixfold ring accepts single TMA guest molecules in different positions until the saturated monolayer is reached. Therefore entropy doesn't tend to zero in close packed structure. (2) The phase composed of sixfold rings of TMA doesn't appear and adlayer undergoes only the first-order phase transition from disordered lattice gas to close packed structure. The model structures of self-assembled adlayer of TMA are analogous to real ones.

It is interesting that the transition to more complex models of self-assembled adlayer of TMA which approach to real size relation between molecule and surface atoms, for example model with nearest neighbor exclusion and next-nearest neighbor attractions, doesn't lead to qualitative changes in phase behaviour. Thus, to understand the phase behaviour of such complex system more deeply it is enough to study the simplest model costructed in this work.

References

[1]. H. Liang, Y. He, Y. Ye, et al., Coord. Chem. Rev. 249 **(2005)** 2959.
[2]. M. Hietschold, M. Lackinger, S. Griessl, et al., Microelectronic Engineering 82 **(2005)** 207.
[3]. J.C. MacDonald, G.M. Whitesides, Chem. Rev. 94 **(1994)** 2383.
[4]. A. Dmitriev, N. Lin, J. Weckesser, J.V. Barth, K. Kern, J. Phys. Chem. B 106 **(2002)** 6907.

PP-I-22

USING LAWS OF THERMODYNAMICS FOR MATHEMATICAL MODEL OF ALKYLATION PROCESS DEVELOPMENT AND INVERSE KINETIC PROBLEM SOLVING

Fetisova V.A., Shnidorova I.O., Belinskaya N.S., Ivashkina E.N.

Tomsk Polytechnic University,
Lenin av. 30, Tomsk, Russia, 8(3822)563443, shnidorova@sibmail.com

Stage of alkylation of benzene with olefins C_{10} - C_{14} is an integral part of the production of synthetic detergents (SD). The structure of linear alkyl benzene (LAB) obtained at this stage affects both biodegradability of detergents produced from them, and their solubility and cleaning performance, so the efficiency of this stage of production determines the yield and quality of the final product.

From the literary data [1] it is known that the production of detergents of the highest quality is possible on the basis of the LAB corresponding to the requirements of GOST of bromine index, the percentage of the linear isomer in the output stream, as well as the number of alkylbenzenes containing side chain of 12 carbon atoms. Quality of heavy alkylate (HA) - another commodity product of alkylation process - is determined by the bromine number, which is an indication of the content of unsaturated compounds of the product flow.

Thus, the alkylation of benzene with higher monoolefines is a complex multifactor system. Its optimization can be carried out with use of mathematical model that takes into account the concentration of as more as possible number of individual components (to enable the identification and improvement of quality of products) [2,3]. Development of a computer modeling system involves a significant degree of process detailing: separation of hydrocarbons in the scheme of transformations according to the number of carbon atoms in the molecule, degree of isomerization, position of double bond in the molecule of olefin. Such an approach would inevitably lead to the complication of the mathematical description of the process and to significant increase in the number of unknown kinetic parameters, in our case, up to 88. However, the establishment of quantitative relationships between the reactivity of hydrocarbons and the laws of thermodynamics can greatly simplify the solution of the inverse kinetic problem.

In this context, we developed an algorithm search of the kinetic parameters of the model, based on:

– Reduction of the number of unknown parameters to 44 using the thermodynamic relation $Kp = \frac{k_{0,i}}{k_{0,-i}} = e^{\frac{-\Delta G}{RT}}$;

– establishing of pre-exponential factors dependence on the number of carbon atoms in a molecule on the basis of expression $Kp = \frac{k_{0,i}}{k_{0,-i}} = e^{\frac{-\Delta G}{RT}}$ and reduction of the number of unknown parameters to 12;

– reduction of the number of unknown parameters to 6 by marking out the 6 principal types of carbocations and, accordingly, the 6 main groups of reactions;

– grouping of pre-exponential factors on the basis of pre-appraised values and their expression through 2 benchmarks.

The final values of kinetic parameters are determined with use of search engine optimization techniques.

Thus found the values of kinetic parameters are used as the basis of developed and programmatically implemented mathematical model of alkylation process. In the end, developed computer modeling system allows optimum technological conditions for each specific type of raw material selecting to ensure high quality and stable yield of LAB product.

Thus, taking fundamental physical and chemical laws of reagents transformation and sufficiently detailed mechanism of the process into account of makes a mathematical model of alkylation process sensitive to the composition of feedstock and provides its predictive ability, so, it becomes possible to optimize the process by maintaining of optimal process parameters, calculated with use of the model. Using the laws of thermodynamics makes it easy to solve the inverse kinetic problem, even with considerable detail of the mathematical description.

References:

[1]. Bannov P. G. Processes of oil refining. - M.: TsNIITEneftehim, 2001. - 625 pp.

[2]. Veronica A. Fetisova, Edward V. Malahov, Elena N. Ivashkina Alkylation reactor modeling in linear alkylbenzenes production //Abstracts XVIII International Conference on Chemical Reactors CHEMREACTOR-18 - Malta, September 29 – October 3, 2008. - Novosibirsk: Institute of Catalysis behalf GK Boreskov, SB RAS, 2008. - 315-316 pp.

[3]. Fetisova V.A., Ivashkina E.N., Ivanchina E.D., Kravtsov A.V. Development of mathematical model of benzene alkylation with higher olefins process // Catalysis in Industry, 2009, - № 6. - 27-33 pp.

SELF-OSCILLATIONS DURING OXIDATIVE CARBONYLATION OF UNSATURATED COMPOUNDS

Gorodsky S.N., Temkin O.N., Bruk L.G.

Lomonosov State Academy of Fine Chemical Technology (MITHT), Moscow,
Gorodsky@yandex.ru

The report is devoted to review of the reactions by metal complexes proceeding in a self-oscillatory mode, which was discovered on the faculty of Basic Organic Synthesis of MITHT last years. For last 50 years many oscillating reactions in different areas of chemistry and biochemistry [1] were revealed.

We managed to find oscillatory modes in a number of carbonylation reactions of unsaturated compounds. The first oscillatory process we discovered was a reaction of acetylene carbonylation in the system $PdBr_2$ – PPh_3 – HBr – butan-1-ol – dimethylsulfide.

There were periodic changes of gas mixture absorption rate, color of catalytic solution, values of electric potential and pH found [2]. At research of alkynes oxidative carbonylation reaction on ≡C-H bond it was shown, that reaction process in catalytic system PdI_2–KI–MeOH proceeds in an oscillatory mode [3-5] (Fig.1).

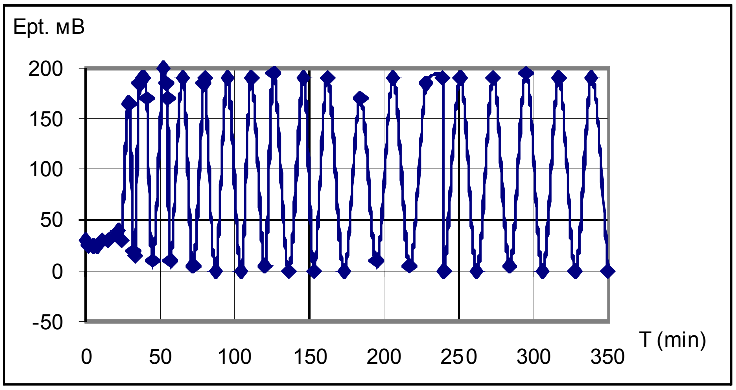
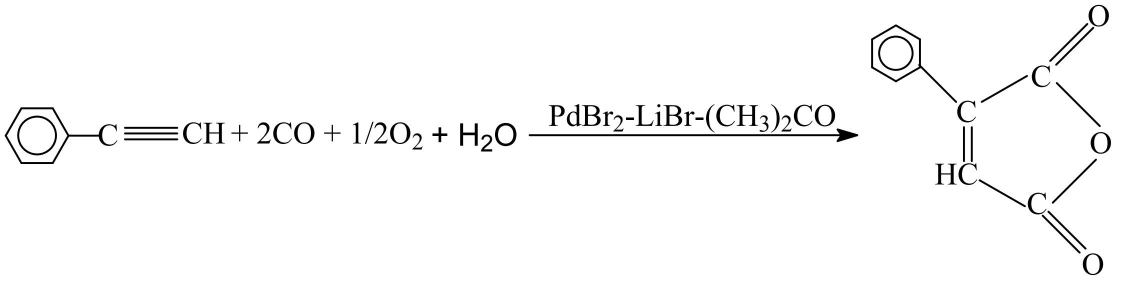


Fig. 1. Oxidative carbonylation of methylacetylene: $[PdI_2]_0$ = 0,01 M, $[KI]_0$ = 0,4 M, $[CH_3C{\equiv}CH]_0$ = 0,5 atm, CO/O_2 = 1,5

The critical behavior of acetylene oxidative carbonylation reaction to maleic anhydride in the system $PdBr_2$-LiBr-CH_3CN was also discovered. At ratio P_{CO}:P_{C2H2} > 3 and P_{O2} up to 0,2 atm the main product is succinic anhydride, at ratio P_{CO}:P_{C2H2} < 3 – maleic anhydride [6].

Recently the oscillations of E_{Pt} and pH of reaction solution in the system LiBr-$PdBr_2$-H_2O-aceton-phenylacetilene (or methylacetylene) were found (1); the oscillations of intermediates concentrations in the system PdI_2-KI-MeOH-dimethylethynil carbinol and some other processes were also discovered (Fig. 2).



(1)

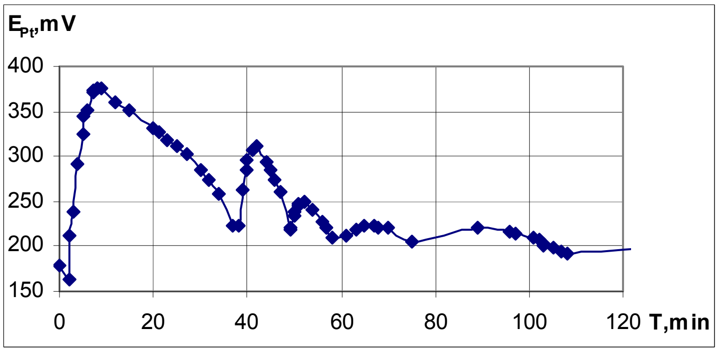


Fig. 2. Oxidative carbonylation of phenylacetylene in system LiBr-$PdBr_2$-H_2O-acetone LiBr=0,2M; $PdBr_2$=0,01M; PhA=0,1M; H_2O = 0,75M; $V_{(CH3)2CO}$=10мл; $[CO]_0$: $[O_2]_0$ = 1:1

Many well-known and adequately investigated systems are described by linear mechanisms until now; it can testify that no one really searches in these mechanisms nonlinear effects. On our deep opinion, time has come to make it.

References

[1]. R.J. Field, M. Burger, Oscillations and Travelling Waves in Chemical Systems, Wiley, New York, **1985**.

[2]. G.M. Shul'akovsky, O.N. Temkin, N.V. Bykanova, A.N. Nyrkova, in book: Chemical kinetics in catalysis: Kinetic models of liquid-phase reactions, Chernogolovka: IPC, **1985**, 112.

[3]. A.V. Malashkevich, L.G. Bruk, O.N. Temkin, J. Phys. Chem., A, **1997**, 101, 51, 9825.

[4]. S.N. Gorodsky; A.N. Zaharov; A.V. Kulik; L.G. Bruk; O.N. Temkin; Kinetic and Catalysis, **2001**, 42, 2, 285-293.

[5]. S.N. Gorodskii, E.S. Kalenova, L.G. Bruk, O.N. Temkin, Russ. Chem. Bull., **2003**, 52, 7, 1534 - 1543.

[6]. L.G. Bruk, I.V. Oshanina, A.S. Zakieva, A.P. Kozlova, O.N. Temkin, Kinetics and Catalysis, **1998**, 39, 2, 183 – 186.

Acknowledgements

These works were financially supported by RFBR (grants № 05-03-33151 and № 09-03-01072).

ORGANOCYCLOSILOXANE POLYMERIZATION ACTIVATED BY AROMATIC ISOCYANATES BY A MACROINITIATOR

Gumerov A.M., Davletbaeva I.M., Galjautdinova A.F., Ahmetshina A.I.

Kazan State Technological University, 420015, K. Marks Str., 68, Kazan, Russia
gumerov_a@mail.ru, davletbaeva09@mail.ru

Copolymers based on octamethylcyclotetrasiloxane (D_4), aromatic isocyanate by a macroiniator, which is polyether containing end potassium- alcoholate groups and hydroxyl groups (PPG-K), were synthesized. Both bifunctional 2,4-toluene diisocyanate (TDI) and monofunctional phenyl isocyanate (PIC) were used as aromatic isocyanates.

The mechanism of organocyclosiloxane opening on a macroinitiator activated by aromatic isocyanates was investigated, the mathematical modeling of reaction kinetics being used. Polymers obtained in toluene by the interaction of PPG-K, PIC and D_4 were separated by evaporation, then they were analyzed by means of infared spectroscopy. In infared spectra, when there is slight excess of PIC, the bands in the area of 1651 cm^{-1}, corresponding to the fluctuating of C=N bond, and the arm in the area of 1210 cm^{-1}, conditioned by fluctuating of C-O-C bond (included into polyisocyanate group having acetal characteristics (O-polyisocyanates) are observed. If mole fraction of PIC is further increased, phenyltriisocyanurate crystals are separated out after a while when the interaction product is dissolved.

To study the regularities of polymer (obtained by D_4 polymerization activated by aromatic isocyanates) molecular characteristics changing the dependences of intrinsic viscosity on polymer concentration were measured. Monofunctional phenylisocyanate was used as aromatic isocyanurate. The model studies were also performed by a macroinitiator when either PIC or D_4 was not incorporated into the reaction system. It turned out that intrinsic viscosity of polymers synthesized on the base of PPG-K, PIC and D_4 exceeds substantially the intrinsic viscosity obtained not only for model systems but obtained for commercial siloxane oligomers as well. It is determined that the microphase separation proceeds in polymer, polyether, siloxane and triisocyanurate components taking part in it.

SYNTHESIS OF ETHYLENE OXIDE IN A MICROREACTOR: ELUCIDATING THE REACTION MECHANISM THROUGH DETAILED KINETIC MODELLING

José Rafael Hernández Carucci[1], Mauricio Roche[1], Hongfan Guo[2], Johan Wärnå[1], Kari Eränen[1], Markku Leskelä[2], Tapio Salmi[1], Dmitry Yu. Murzin[1]

[1]Laboratory of Industrial Chemistry and Reaction Engineering, Process Chemistry Centre, Åbo Akademi University, Biskopsgatan 8, FI-20500, Turku/Åbo, Finland
[2]Laboratory of Inorganic Chemistry, Department of Chemistry (A.I.Virtasen aukio 1) P.O. Box 55, FI-00014 University of Helsinki, Finland

Ethylene oxide (EO) is one of the most important organic intermediates with an annual global production of ca. 19 million metric tons. EO is produced by the selective partial oxidation of ethylene, with a total heat of reaction between -350 to -550 kJ/mol, causing hot spots and heat removal problems in conventional reactors. The transport of EO to long distances poses a safety risk. Furthermore, shipping costs are expected to grow in the future. Thus, a tailored, on-site production of EO becomes an attractive option with the aid of suitable, selective heterogeneous catalysts. This requires, however, advanced reactor technology, in which the classical problems of scale-up and operability are avoided. Such a technology is provided by microstructured devices, particularly gas-phase microreactors, which are inherently safe and have very good operability properties [1,2]. Microreactors are still a relatively novel technology in chemistry, but already many advantages over conventional reactor design have been identified. Many of these advantages are related to the issue, that even though the chemistry itself is scale-independent, transport phenomena are not. In microengineered systems, mass and heat transfer are intensified: the decrease of the characteristic dimensions lead to the increase of the surface-to-volume ratio enhancing the mass and heat transfer between the surfaces and the fluid. Moreover, the intrinsic safety provided by these reactors allows the operation under explosive regime, e.g. ethylene in pure oxygen, conditions not possible to obtain in conventional laboratory vessels. A lot of research is done on catalytic gas-phase processes in microdevices, but kinetic modelling is often missing. In this work, we present a systematic approach to a very precise kinetic modelling of data obtained from a microreactor. So far, silver supported on alumina has been the catalyst of choice for the synthesis of EO. However, the recent growing interest in gold-supported catalyst has opened a window of possibilities for many chemical transformations. In this work, we have compared a traditional silver catalyst with a Au/TiO_2 one. The silver/α-alumina catalyst was prepared by thermally decomposing γ-alumina and further silver impregnating it with Ag by the incipient wetness method. The catalyst was succesively washcoated in the microplates as described in [3]. The Au/TiO_2 catalyst was deposited on the microplates by atomic layer deposition (ATD). A gas-phase microreactor was used for the synthesis of EO using a total gas flow rate of 6 ml/min. The varied parameters for the kinetic modelling were pressure (1-5 bar), oxygen and ethylene concentrations (1-25 vol.%) and temperature (220-300 °C). The effluent gases were analyzed by a Agilent 3000A Micro. Conversions of ethylene up to 40% were achieved at high pressures (5 bar). The selectivity towards ethylene oxide for silver-alumina catalysts reached 70%. As Au/TiO_2 was used, activities up to 40% and selectivities up to 60% were reached. Fig. 1 presents the conversions and selectivities towards ethylene oxide when using silver/alumina microchannels at atmospheric pressure. Ethylene and oxygen concentrations had a positive effect on both the rate of ethylene oxide formation and carbon dioxide formation. For the kinetic modelling a steady-state plug-flow reactor model was assumed. The influence of the reaction products and internal diffusion limitations were considered but found to be negligible.

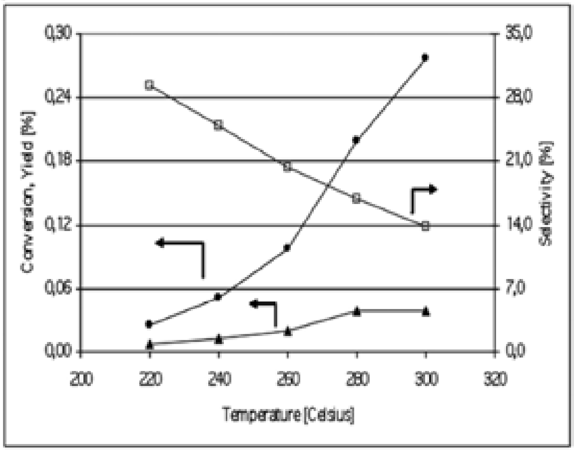


Fig. 1. Conversion and selectivity towards ethylene oxide over Ag/α-Al_2O_3 coated microchannels. 20 vol.% ethylene, 10 vol.% oxygen, total flow 6.0 ml/min, p = 1 bar.

A competitive Langmuir-Hinshelwood model was used with the surface reaction between adsorbed ethylene and dissociatively adsorbed oxygen as the rate-limiting step. The kinetic fit of the model and the parity plots (degree of explanation of 97%) are presented in the full manuscript.

References

[1]. Gavriilidis, A.; Angeli, P.; Cao, E.; Yeong, K. K.; Wan, Y. S. S. Technology and applications of microengineered reactors. *Chem. Eng. Res. Des.* **2002**, *80*, 3.

[2]. Stankiewicz, A. I.; Moulijn, J. A. Process intensification: Transforming Chemical Engineering. *Chem. Eng. Prog.* **2000**, *96*, 22.

[3]. Stefanescu, A.; van Veen, A.C.; Mirodatos, C.; Beziat, J.C.; Duval-Brunel, E. Wall coating optimization for microchannel reactors, *Catal. Today* **2007**, *125*, 16.

OPTIMUM KINETICS FOR POLYSTYRENE BATCH REACTOR BY NEURAL NETWORKS APPROACH.

Hosen M.A., Hussain M.A., Mjalli F.S.

Chemical Engineering Department, University of Malaya, Malaysia,
E-mail: Anwar.buet97@gmail.com

The process of polymerization is subjected to very complicated reactions with nonlinear behaviour. Due to the non-linear time varying of the process, the characteristics of the polymerization reactions are often partially known and the conventional modelling approach based on the mass and energy balance equations is quite limited. This paper presents a neural network approach that generates kinetic parameters of polymerization. These parameters are thus used in the conventional mechanistic model to describe mass and heat transfer phenomena. The neural network model has been adjusted on the basis of experimental data carried out on a batch reactor. The experimental validation revealed that the new model has a high prediction capabilities compared to the reported models. With proper scaling of the developed model, it can be used for further system analysis and control, which will be the topic for the next phase of this research.

Key words: Polystyrene batch reactor; Modeling polymerization reactor; Free radical; Kinetic Parameters; Neural network.

KINETICS OF CO METHANATION OVER SUPPORTED NICKEL CATALYSTS

Huan N.M.[1], Loc L.C.[1], Tri N.[1], Thoang H.[1], Gaidai N.A.[2], Nekrasov N.V.[2], Agafonov Yu.A.[2], Lapidus A.L.[2]

[1] *Institute of Chemical Technology, VAST, Ho Chi Minh, Vietnam*
[2] *N.D. Zelinsky Institute of Organic Chemistry RAS, Moscow, Russia*
gaidai@server.ioc.ac.ru

The reaction of methanation is used to remove CO from feeding gases in many industrial processes, such as, coal gasification, ammonia synthesis and hydrogen production. Although there are many publications on CO methanation over nickel catalysts, there is no single opinion on kinetics and mechanism of this reaction. Main distinctions of presented works on kinetics of CO methanation consist in the nature of intermediate compounds (different oxygen compounds of CO or carbon formed at CO dissociation) taking part in the slow step of the process. In previous studies [1, 2] we have found some optimal compositions of catalysts with NiO supported over TiO_2, Al_2O_3, SiO_2 as well as γ-Al_2O_3 + SiO_2 (mechanical mixture) for the CO methanation. They are the following: 7.5(wt.%)NiO/TiO_2, 38NiO/Al_2O_3, 30NiO/SiO_2 and 25NiO/30%γ-Al_2O_3+70%SiO_2, of which two samples 7.5NiO/TiO_2 and 38NiO/Al_2O_3 have the most activity. Kinetics of the CO methanation over two catalysts has been presented in this work. The industrial application of nickel-alumina catalysts can be more preferable than nickel-titania ones. Catalysts were prepared as described in [1]. The catalysts were investigated by methods BET, XRD, TPR and hydrogen pulse titration. Kinetic studies of the reaction were carried out in a gradientless circulating reactor at atmospheric pressure; reaction temperatures were 180, 200, 220 and 240°C. The values of initial partial pressures of carbon monoxide (P_{CO}^{o}), hydrogen (P_{H2}^{o}), water steam (P_{H2O}^{o}) and methane (P_{CH4}^{o}) were changed in the ranges (atm): 0.05-0.30; 0.17-0.67; 0-0.22 and 0-0.30, respectively. In these conditions the extents of CO conversion were altered from 9% up to 95%. It was shown that the reaction proceeded in the kinetic region over catalyst particles less 1 mm.

Surface characteristics of the catalysts are presented in Table. The values of average pore size TiO_2 and Al_2O_3 are respectively 28Å and 24Å, that easies the reactants and products to diffuse. The values of Ni crystals size in both the catalysts are approximately identical and suitable for this reaction (10÷20nm).

Table

Specific surface area (S_{BET}) of the catalysts, surface area of Ni on 1g catalyst (S_{Ni}), surface area of 1g Ni (S'_{Ni}), diameter of Ni crystals (d_{Ni}), dispersity of Ni on catalyst surface (γ_{Ni}), maximum of reduction temperature (T_{max}), area of reduction peaks (S_{max}) and quantity of reduced centers (N_{Ni2+}) per 1g catalyst

Catalyst	S_{BET}, m²/g	S_{Ni}, m²/g	S'_{Ni}, m²/g	d_{Ni}, nm	γ_{Ni}, %	T_{max} °C	S_{max}	N_{Ni2+}
7.5%NiO/TiO_2	34	4	68	15	10	543	$2,3.10^5$	$6,8.10^{20}$
37.7%NiO/Al_2O_3	125	20	54	19	8	492	$5,2.10^5$	$15,5.10^{20}$

The following conclusions can be derived from the obtained experimental data over two catalysts: 1) the kinetic equation must be not a simple exponential one, but of a fraction form, expressing the inhibition at least by one of the products, 2) P_{CO} and P_{H_2} must be present in both numerator and denominator of the equation and the value of the exponent of P_{CO} in the numerator is smaller than in the denominator. P_{H_2O} is present only in the denominator with the exponent value of unit, P_{CH_4} is absent in the kinetic equation. The rate of the reaction (r) over two catalysts is described by the same kinetic equation:

$$r = \frac{k_1 P_{CO} P_{H_2}^{0,5}}{\left(P_{H_2}^{0,5} + k_2 P_{CO} + k_3 P_{H_2O}\right)^2},$$

but the values of constants are different. The step-scheme of the process was proposed. The slow step is the interaction of the adsorbed CO and hydrogen atom. The kinetic equation can be derived from this step-scheme assuming that the reaction proceeded in the region of high coverage of the nonuniform catalyst surface [3].

References:

[1]. Luu Cam Loc, Nguyen Manh Huan, Ho Si Thoang. *J. Chemistry* **2007***,* 45, 33.

[2]. Nguyen Manh Huan, Luu Cam Loc, Nguyen Kim Dung, Ho Si Thoang. *Advances in Natural Sciences* **2008**, 9, 69.

[3]. Kiperman S.L. *Introduction to Kinetics of Heterogeneous Catalytic Reactions. Nauka, Moscow.* ***1964****. 608 PP.*

AUTOWAVE MODES OF CRYOPOLYMERIZATION IN SYSTEM WITH FILLERS: A PROBLEM OF CREATING POLYMER COMPOSITES AT ULTRALOW TEMPERATURES

Kiryukhin D.P., Kichigina G.A., Barelko V.V.

Institute of Problems of Chemical Physics,
Russian Academy of Sciences, pr. Akademika Semenova 1,
Chernogolovka, Moscow oblast, 142432 Russia
E-mail: kir@icp.ac.ru

Autowave modes of transformation in preliminarily radiolyzed or photoirradiated solid systems near absolute zero have been detected previously [1,2]. A chemical reaction is initiated by local brittle fracture of a long solid sample at 4.2–77 K. The development of the reaction process is ensured by layer-by-layer dispersion of the sample because of temperature or density gradients arising in the reaction, and the chemical transformation propagates layer by layer as a traveling wave throughout the sample. The brittle fracture of the radiolyzed solid matrix of reactants is a determining factor both at the initiation stage and during the auto-wave process on the freshly forming surface. The fracture of the sample is obviously controlled by its strength. The stronger the solid matrix of reactants, the more difficult to trigger the autowave mode of chemical transformation. In a wide range of objects used for studying auto-wave modes of solid-phase cryotransformations, a significant place is occupied by polymerization and copolymerization.

We investigated specific features of autowave modes of polymerization cryotransformation in a monomer matrix with filler. As a model object, we chose acetaldehyde, the autowave solid-phase polymerization of which without filler was studied in sufficient detail. In this work, we explored the effect of addition of fine aluminum oxide powder on the development of the autowave process of acetaldehyde cryopolymerization at 77 K. The postirradiation polymerization of the system occurs within the same temperature range as that for pure acetaldehyde, the effective activation energy is 7.0 kJ/mol, and the polymer yield is ~50%. Consequently, aluminum oxide powder can be considered an inert additive causing no changes in the kinetics of thermally activated post-polymerization of acetaldehyde. For the autowave mode of transformation initiated by local mechanical perturbation at 77 K, unlike the thermally activated process (slow heating of γ-preirradiated sample), the characteristics of the processes in pure acetaldehyde and in the mixture with aluminum oxide differ noticeably. First of all, the critical γ-preirradiation dose necessary for triggering an acetaldehyde polymerization wave in the Al_2O_3–acetaldehyde system is much higher (600 kGy) than that for pure acetaldehyde (300 kGy). The measured wave velocities in the Al_2O_3–acetaldehyde mixture are lower than those in pure acetaldehyde: at the critical irradiation dose, they are 3 and 5 mm/s, respectively, and at a dose of 900 kGy, they are 14 and 38 mm/s, respectively According to theory [3], the increase in the critical irradiation dose necessary for triggering the autowave mode of transformation and the decrease in the reaction traveling wave front velocity, which were observed for acetaldehyde with filler, are indicative of strengthening of the matrix, i.e., an increase in the critical temperature gradient destroying the sample. The above data demonstrate that addition of aluminum oxide powder to acetaldehyde leads to strengthening of the frozen solid system, i.e., to difficulties in triggering the autowave mode of polymerization. However, an increase in the preirradiation dose gives rise to a traveling wave of transformation in the monomer–filler system. Thus, the results obtained for the model Al_2O_3–acetaldehyde system confirmed the possibility of developing a technology for producing composite materials at low (space) temperatures in traveling wave mode using space and solar radiation for activating the frozen monomer matrix. It is of interest to study the effect exerted on the autowave process by fillers of other types (fiberglass woven reinforcing components, metal grids, catalytically active fillers, etc.). These fillers may have a significant effect on the development of the autowave process. On the one hand, the strengthening suppresses cracking and decreases the velocity of wave propagation throughout the sample, but on the other, the presence of a component that increases the effective thermal conductivity of the system may increase the reaction rate. It is also of interest to use catalytically active fillers, which allow one to create composite materials at high rates of autowave transformation. And, of course, it is necessary to choose monomers that would be suitable for creating composites with required properties by autowave transformation at low temperatures.

References

[1]. Barelko, V.V., Barkalov, I.M., Goldanskii, V.I., et al., *Adv. Chem. Phys.*, 1988, vol. 74, pp. 339–384.
[2]. Kiryukhin, D.P., Barkalov, I.M. *Usp. Khim.*, 2003, vol. 72, no. 3, pp. 245–261.
[3]. Barelko, V.V., Barkalov, I.M., Vaganov, D.A., et al., *Khim. Fiz.*, 1983, vol. 2, no. 3, pp. 980–984.

PP-I-29

NUMERICAL INVESTIGATION OF NANOPARTICLES TRANSFER TO THE WALL OF HIGH-TEMPERATURE REACTOR

Kolesnikov A., **Moropeng L.**

Tshwane University of Technology, Pretoria, South Africa, kolesnikova@tut.ac.za

Inorganic nanopowders (particle size in the range 10-1000 nm) are finding significant applications in a number of new advanced technologies. One of the attractive methods of nanopowders manufacturing at high production rate (hundreds of kilograms per hour) is a high-temperature gas phase synthesis in plasmachemical reactors or flame reactors [1,2].

The direct gas phase chemical reaction of precursor vapor to form particles and the ease of separation of the particulate products from the gas make high-temperature gas phase reactors an attractive device for control of particle size distribution, which is on of the most important characteristic of nanopowders.

However, proper operation of reactors requires better understanding of the role of various factors, affecting the formation of particle size distribution.

Formation of nanoparticles can be considered in the following schematic manner. The gaseous precursors undergo homogeneous gas phase reactions forming condensable products, whose transition to the solid or liquid phase is initiated by homogeneous nucleation. Coagulation (coalescence) of nuclei and particles contribute to the further development of the particle size and number concentration. In high-temperature reactor with cooled walls the coagulation occurs under conditions of high temperature gradients, inducing thermophoresis [3]. The presence of turbulence in the flow also introduces turbophoresis. These two factors are responsible for the nanoparticle transfer to the reactor's wall. As a result of thermophoretic and turbophoretic forces action, the particle number concentration in gas flow decreases, affecting the coagulation rate and further the particle size distribution.

The objective of the present paper is to analyze spatially two-dimensional aerosol dynamics for the high-temperature gas phase process in which the size distribution function (and average size) vary both in axial and in radial directions in a tubular reactor. Particular attention is given to the influence of thermophoresis and turbophoresis. The developed mathematical 2D stationary model incorporating heat, mass, momentum transfer and aerosol dynamics was solved with the help of commercial CFD solver FLUENT. The simulation results are presented in a form of spatial distributions of temperature, velocity, pressure, concentrations, particle average size in 2D tubular gas phase reactor. Comparison of simulation results with previously published data is given, and sensitivity of model predictions to the model parameters is discussed.

References

[1]. Xiong, Y., Pratsinis, S. E. “Gas Phase Production of Particles in Reactive Turbulent Flows”, *J. Aerosol Sci.*, (**1991)**, 12, 637-655.

[2]. Kolesnikov, A. V., Alexeev, N., Samokhin, A. "Controlled Synthesis of Alumina Nanoparticles in a Reactor with Self-Impinging Plasma Jets" *International Journal of Chemical Reactor Engineering,* (**2007**) Vol. 5: A95.

[3]. Gomez, A., Rosner, D. E. “Thermophoretic Effects on Particles in Counterflow Laminar Diffusion Flames “,*Combustion Science and Technology*, (**1993**), 89, 335 – 362.

[4]. Pyykönen, J., Jokiniemi, J. “Model studies of deposition in turbulent boundary layer with inertial effects”. *Proceedings of the VIII Finnish National Aerosol Symposium*. (**2001)** Report Series in Aerosol Science 54, Finnish Association for Aerosol Research. 28−38.

SPECIAL FEATURES OF METHANOL CONVERSION OVER ZEOLITES WITH A HIGH SILICA MODULUS

Korobitsyna L.L., Ulzii B., Vosmerikov A.V.

Institute of Petroleum Chemistry, Siberian Branch of the Russian Academy
of Sciences, 634021, 4, Akademichesky Avenue, Tomsk, Russia
E-mail: kll@ipc.tsc.ru

In recent years, the interest in the process for conversion of methanol into dimethyl ether, high-octane gasolines and low olefins has increased due to oil stock shortage and increased cost. High silica zeolites of the ZSM-5 type are effective catalysts for this process. The methanol conversion over pentasyl-type zeolites proceeds through the stage of dehydratation of methanol into dimethyl ether with further conversion of the latter into a mixture of hydrocarbons according to the scheme: MeOH → DME → olefins → aromatics and paraffins. Catalyst's acidity is an important factor affecting its active and stable operation. A method to control the zeolite acid properties is by varying the SiO_2/Al_2O_3 molar ratio in the zeolite framework.

This work discusses the results of investigation into catalytic activity and stability of zeolites with a silica modulus of M=60-500 in the reaction of conversion of methanol into hydrocarbons. High-silica zeolites were produced via hydrothermal crystallization of alkaline alumosilicagels at 175 ^{o}C for 20-48 h. Hexamethylendiamine was used as a structure-forming agent. The data of infrared spectroscopy (IR) and X-ray diffraction (XRD) analysis indicate that the zeolites obtained are characterized by a high degree of crystallinity and are referred to as zeolites of the ZSM-5 type. Their acid properties are studied by the method of temperature programmed desorption (TPD) of ammonia. All the samples synthesized have two types of acidic centers: weak and strong acidic sites. The acid properties of zeolites substantially depend on the content of Al atoms in the zeolite framework. The strength and concentration of acidic sites in the zeolites with M=60-200 are considerably higher than those in the samples with a lower Al content in the crystal lattice.

Catalytic activity of the zeolites was investigated during methanol conversion in a flow type installation with a stationary catalyst layer ($V=5$ cm^3) at 390 °C, space velocity 1 h^{-1}, and atmospheric pressure. The conversion of methanol over every catalyst under study is found to be 100%. The test results are given in Table. The data show that the distribution of reaction products substantially depends on the SiO_2/Al_2O_3 molar ratio in the zeolite framework. With an increase in the zeolite silica modulus, a considerable decrease in the yield of low alkanes and increase in the yield of formed alkenes C_2-C_4 is observed.

Table *Conversion of methanol into hydrocarbons over zeolites*

Concentration, %	Silica modulus							
	60	100	200	300	400	400^{***}	500	500^{***}
Total C_1-C_4	51.7	49.7	48.7	37.9	36.9	34.4	40.0	40.2
alkanes C_1-C_4*	86.1	72.5	55.4	53.4	50.1	51.5	46.5	51.0
alkenes C_2-C_4*	4.1	15.6	25.8	26.3	28.9	22.7	29.7	31.1
Total C_{5+}	46.6	50.1	50.9	61.9	62.7	65.2	59.8	58.6
alkanes C_{5+}**	0.1	0.8	1.2	1.4	1.9	0.9	2.8	0.9
alkenes C_{5+}**	0.2	0.6	1.6	3.4	5.5	3.1	8.8	4.1
i-alkanes C_{5+}**	3.1	5.3	9.0	17.8	22.9	16.9	26.2	18.3
aromatics**	93.4	89.5	84.1	73.5	60.8	74.1	55.5	71.1
Service time, h	41	103	430	723	509	828	110	260

Note. * – content of gas-phase products; ** – content of liquid-phase products; *** – double decationisation.

The aromatic hydrocarbons are the main components of catalysates produced over zeolites with high silica modulus. The yield of aromatics appreciably decreases with an increase in the zeolite silica modulus. In particular, if the content of aromatic hydrocarbons in liquid products obtained over the sample with M=200 is 84.1%, their concentration in the catalysate formed over the zeolite with M=400 is as low as 60.8%. The fraction of isoalkanes in the liquid phase formed substantially increases with an increase in the zeolite silica modulus. Specifically, the yield of isoalkanes over catalysts with M=200 and M=400 is 9.0 and 22.9%, respectively. It is well known that the lower is the Al content in a zeolite, the stronger the sodium cations inhibit its catalytic activity. This work focuses on catalytic activity and stability of doubly decationized zeolites with M=400 and M=500. Double decationization of zeolites decreases the yield of low alkenes and isoalkanes and increases the formation of low alkanes and aromatic hydrocarbons. The zeolite catalyst with silica modulus 300 is characterized by the maximum time of stable operation. Double decationization allows increasing the time between the regenerations of catalyst with M=400 from 509 up to 828 h and for catalyst with M=500 from 110 to 260 h, respectively.

Thus, zeolites with silica modulus more than 100 exhibit high catalytic activity and stability during the conversion of methanol into hydrocarbons. With increasing the zeolite silica modulus, the part of olefins present in the gas phase formed also increases, while the content of aromatic hydrocarbons in the liquid reaction products decreases. It has been found out that double decationization of zeolites increases the duration of their stable operation during the reaction of conversion of methanol.

PP-I-31

QUANTUM-CHEMICAL RESEARCH OF REACTION KINETICS IN COMBUSTION PROCESSES

Kukueva V.

Academy of Fire Safety named after Chernobyl Heroes
Cherkassy, Ukraine, kukueva@yahoo.com

In organic chemistry nearly all chemical processes seem to proceed through a set of reaction steps which involve radicals and/ or other neutral reaction intermediates. Such is especially the case in combustion chemistry. In recent years, many kinetic studies of hydrogen oxidation have concentrated on a single set of experimental results obtained either in shock tubes, or in flow reactors or in flames; these have been simulated using a detailed kinetic mechanism. There have been a very large number of measurements made on the reaction between hydrogen and oxygen. These include flame speed measurements, burner-stabilized flames in which species profiles are recorded, shock tube ignition delay times, and concentration profiles in flow reactor studies [1]. It was shown, that main role in the flame spread velocity play some radicals to take part in the chain carrier growth reaction steps. They were named active centers of flame and for their scavenging could be directed the inhibitor action [2].

This study aims to simulate these experiments and also the data about control of combustion velocity by small amount of galogenated inhibitors. A fundamental understanding of the chemistry of these agents in hydrogen flames should facilitate identification of desired characteristics of effective agents. The focus of the task restricted to the chemistry involving only fluorine containing hydrocarbons, because they was accepted as suitable alternative fire extinguishing agents as ozone friendly replacements for current commercial halons.

It was shown in the previous paper [3], that $CF_3^{\bullet}$ radical is one the most effective scavenging agent for the active centers of flame $O^{\bullet}$, $H^{\bullet}$, $OH^{\bullet}$. Therefore the more amounts of this particles would form during thermal decomposition of fire extinguishing substances the more effective inhibition action would appear for this agents. The calculation by nonempirical ab initio method using Gamess 94 codes in the 6-31 G* basis set were performed to research of $CF_3^{\bullet}$ destruction from fluorine containing hydrocarbons. The calculation results has been presented in the table.

The destruction ways of CF_3• from fluorinated hydrocarbons	E_{tot} (a.u.)
$CHFCl - CF_3 \rightarrow CHFCl\bullet + CF_3\bullet$	0,1144
$CF_3 - CF_3 \rightarrow CF_3\bullet + CF_3\bullet$	0,1159
$CCl_3 - CF_3 \rightarrow CCl_3\bullet + CF_3\bullet$	0,048
$CBrCl_2\text{-}CF_3 \rightarrow CCl_2Br\bullet + CF_3\bullet$	0,043
$CH_2FCF_3 \rightarrow CH_2F\bullet + CF_3\bullet$	0,1247
$CHF_2 - CF_3 \rightarrow CHF_2\bullet + CF_3\bullet$	0,315
$CF_3Br \rightarrow Br\bullet + CF_3\bullet$	0,0514
$CF_3Cl \rightarrow Cl\bullet + CF_3\bullet$	0,0563
$CH_2{=}CBr\text{-}CF_2\text{-}CF_3 \rightarrow CH_2{=}CBr\text{-}CF_2\bullet + CF_3\bullet$	0,0936
$CH_3\text{-}CF_3 \rightarrow CH_3\bullet + CF_3\bullet$	0,134

As we can see from the table, the destruction energy CF_3• not very large value for all of researched molecules. The less energy has Bromine containing hydrocarbons. It is coincide with the most of experimental and theoretical results. But it is necessary to point that chlorine containing hydrocarbons have close results that in the high temperature flame regime could be negligible. Thus, the reaction pathway were predicted by means of quantum-chemical calculations. It was show also that chlorine and fluorine containing hydrocarbons could be suitable alternative for the bromine containing halons, which forbidden by Montreal Protocol, as stratospheric ozone depletion agents.

Reference

[1]. Nyden M.R., Linteris G.T., Burgess D.R.F., Jr.; Westemoreland P.R., Tsang W., Zachria V.R., Flame Inhibition Chemistry and the Search for Additional Fire Fighting Chemicals.- 467-641 pp. 1994.

[2]. N. Vora, J.E.Siow, N.M. Laurendeau, Chemical Scaveging Activity of Gaseous Suppressants by using Laser-induced Fluorescence Measurements of Hydroxyl. - Combustion and flame 126:1393-1401- 2001.

[3]. Kukueva V.V. Quantum-chemical research of inhibition reaction mechanisms. International Conference on Computational Science, June 23-25, 2008, Krakow, Poland.

PP-I-32

PROCESS DESIGN OF CO_2 RECOVERY: TECHNICAL, ENVIRONMENTAL AND ECONOMIC EVALUATION

Luis P., Albo J., Garea A., Irabien A.

Department of Chemical Engineering and Inorganic Chemistry,
University of Cantabria, Avda. Los Castros s/n 39005, Spain
Fax: +34 942 201591; E-mail: luisp@unican.es

Introduction

Carbon dioxide (CO_2) is one of the major contributors to the greenhouse effect. The power and industrial sectors combined account for about 60% of the global CO_2 emissions [1] and their recovery is a key issue to guarantee the sustainability of industrial processes. Non-dispersive absorption based on membranes has demonstrated to be a suitable and technology for gas recovery [2-6] due to its widespread advantages: controlled interfacial area, independent control of gas and liquid flow rates and it avoids solvent losses due to drops dragging [7, 8]. However, its industrial application is limited by economic considerations that are restricted by environmental targets.

In this paper, a steady state model is developed to describe the mass transfer of CO_2 in a polypropylene hollow fibre module (Liqui-Cel, United States). The model describes the mass transfer in the gas and liquid phases and the corresponding dimensionless equations for both phases have been solved simultaneously. It allows studying the technical viability, in terms of the influence that operating conditions (gas and liquid flow rates) and solvent affinity (H) have on the process efficiency, and also, the economic and environmental limitations can be evaluated in order to determine the range of application of the contactor to fulfil a specific target of CO_2 recovery.

References

[1]. Intergovernmental Panel on Climate Change (IPCC). IPCC special report on carbon dioxide capture and storage. Cambridge University Press (2005).

[2]. Luis P, Ortiz I, Aldaco R, Garea A, Irabien A. Recovery of sulfur dioxide using non-dispersive absorption. Int J Chem React Eng 5: art. no. A52 (2007).

[3]. Yan S, Fang M, Zhang W, Wang S, Xu Z, Luo Z, Cen K. Experimental study on the separation of CO_2 from flue gas using hollow fiber membrane contactors without wetting. Fuel Process Technol 88 (5): 501 – 511 (2007).

[4]. Luis P, Garea A, Irabien A. Sulfur dioxide non-dispersive absorption in N,N-dimethylaniline using a ceramic membrane contactor, J Chem Tech Biotechnol, 83 (11) 1570 – 1577 (2008).

[5]. Katja S, Nijmeijer K, Wessling M. Gas-Liquid membrane contactors for CO_2 removal. J Membrane Sci, 340, 214–220 (2009).

[6]. Luis P, Garea A, Irabien A. Zero solvent emission process for sulfur dioxide recovery using a membrane contactor and ionic liquids, J Membrane Sci, 330 (1 – 2) 80 – 89 (2009).

[7]. Karoor S, Sirkar K. Gas Absorption Studies in Microporous Hollow Fiber Membrane Modules. Ind Eng Chem Res 32 (4): 674 – 684 (1993).

[8]. Gabelman A, Hwang S. Hollow fiber membrane contactors. J Membrane Sci 159 (1-2): 61 – 106 (1999).

Acknowledgments

This research is financially supported by the Spanish Ministry of Science and Technology (Project CTM2006-00317).

PP-I-33

SYNTESIS GAS PRODUCTION ON NICKEL SUPPORTED CATALYSTS IN OXIDATIVE CONVERSION OF METHANE

Maniecki T.P., Bawolak-Olczak K., Mierczyński P., Jóźwiak W.K.

Technical University of Lodz, ul. Zeromskiego 116, 90-924 Lodz, kbawolak@p.lodz.pl

INTRODUCTION

Syngas can be used as a key feedstock for many processes like Fischer- Tropsch synthesis, methanol synthesis and others [1]. The partial oxidation of methane - POM ($CH_4 + ½O_2 \rightarrow CO + 2H_2$) and the oxy-steam reforming of methane - OSR (CH_4 + 0,5-xO_2 + xH_2O → 1-xCO + 2-0,5xH_2) are energy-effective processes for synthesis gas production. The supported Ni/Al_2O_3 catalysts are usually used in the oxidative conversion of methane because of their low cost and good catalytic activity [2]. The disadvantage of this catalytic system is low resistance to carbon deactivation [3].

The aim of this work was modification of Ni/Al_2O_3 catalyst active phase and support to get highly active and selective catalytical materials. The mono 5%$Ni/Cr_2O_3 \cdot Al_2O_3$ and bimetallic 5%Ni-2%$Au/Cr_2O_3 \cdot Al_2O_3$ catalysts were investigated in POM and OSR reactions.

EXPERIMENTAL

The binary co-precipitated support $Cr_2O_3 \cdot Al_2O_3$ was obtain using appropriate mixture of aqueous solution ($Cr(NO_3)_3{\cdot}9H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$) and after removal of excessive water it was dried and calcined at 400°C/4h/air. The supported catalysts 5%$Ni/Cr_2O_3 \cdot Al_2O_3$ and 5%Ni-2%$Au/Cr_2O_3 \cdot Al_2O_3$ were prepared by wet impregnation method of precursors: $Ni(NO_3)_2{\cdot}6H_2O$ and $HAuCl_4$. Catalysts were dried and calcined at 400°C/4h/air [4]. POM and OSR activity tests were carried out in a flow quartz reactor in the temperature range 25-950°C with GC analysis. The physicochemical properties were studied by BET, TPR, XRD and ToF-SIMS techniques.

RESULTS AND DISCUSSION

The POM reaction was investigated for substrates composition $CH_4:O_2$ = 2:1 while OSR with composition of reagents $CH_4:O_2:H_2O$ = 1 : 0,3 : 0,2. The both POM and OSR reaction started about 450°C. The CH_4 conversion was about 20% in the temperature range 450-700°C and C a rapid decrease of methane was observed above 750°. The catalytic properties of 5%Ni/$Cr_2O_3 \cdot Al_2O_3$ and 5%Ni-2%Au/$Cr_2O_3 \cdot Al_2O_3$ systems are presented in table 1. Presented catalysts achieved 100 % and about 20 % of CH_4 conversion at 800 °C respectively in POM and OSR reaction. All samples showed 100% of methane conversion at 900 °C. The loss of activity was below 1% after 24h in partial oxidation of methane, which was mainly caused by formation of carbon deposition. The nickel and nickel - gold catalysts tested in OSR process did not show carbon presence after 24h reaction, but the loss of CH_4 was 5% for 5%Ni/$Cr_2O_3 \cdot Al_2O_3$ probably because of the active phase oxidation.

Table 1. *Catalytic properties of 5%Ni and 5%Ni-2%Au/$Cr_2O_3 \cdot Al_2O_3$ in POM and OSR reaction*

Type of reaction	Catalytic properties	5%Ni	5%Ni-2%Au
		Cr_2O_3 Al_2O_3	
POM	$X_{CH4\ 800°C}$	100	100
	$X_{CH4\ 900°C}$	100	100
	Δx_{24h}	<1	<1
	%C	5	0,3
OSR	$X_{CH4\ 800°C}$	23	19
	$X_{CH4\ 900°C}$	100	100
	Δx_{24h}	5	0
	%C	0,5	<1

CONCLUSIONS

The 5%Ni and 5%Ni – 2%Au/$Cr_2O_3 \cdot Al_2O_3$ systems showed high activity in oxidative conversion of methane (100% at 900 °C) and stability (<5% of the CH_4 conversion after 24h). The various causes of deactivation were observed: carbon deposition formation in POM and active phase oxidation in OSR reaction.

References

[1]. Syngas production and conversion to products – A strategic assessment of the technologies, markets and competitive landscape. Report. www.catalystgrp.com.

[2]. N.V. Vernikovskaya, L.N. Bobrova, L.G. Pinaeva, V.A. Sadykov, I.A. Zolotarskii, V.A. Sobyanin, I. Buyakou, V. Kalinin, S. Zhdanok, Chem. Eng. J., **134 (2007) 180.**

[3]. T.P. Maniecki, K. Bawolak, P. Mierczyński, W.K. Jóźwiak Development of stable and higly active bimetallic Ni-Au catalysts supported on binary oxides $CrAl_3O_6$ for POM reaction, Cat. Lett. **128 (2009) 401.**

[4]. T.P. Maniecki, K. Bawolak, D. Gebauer, W.K. Jóźwiak, „Catalytic activity and physicochemical properties of Ni-Au / Al_3O_6Cr system for partial oxidation of methane to synthesis gas.", Kinetika & Kataliz, **50 (2009) 149.**

STUDY OF THE KINETICS OF THE BUTADIENE POLYMERIZATION PROCESS USING COBALT AND NEODYMIUM CONTAINING CATALYTIC SYSTEMS TAKING INTO ACCOUNT HEAT EXCHANGE AND HYDRODYNAMICS IN A SYSTEM

Manujko G.V., Bronskaja V.V., Aminova G.A., Bashkirov D.V., Diakonov G.S.

The Kazan state technological university, Kazan, Russia, a_guzel@mail.ru

Physical factors can strongly influence an output of polymerization and in many cases appreciably change the certain molecular properties of rubbers. Chemical kinetics considers, mainly, changes of quantitative characteristics of chemical reactions and does not consider physical processes. It uses mathematical models and experimental data about speeds of course of reactions on the basis of which assumptions of the mechanism of reaction are made and concrete rate constants are estimated.

Theoretical bases for controllable synthesis of diene rubbers have developed. Complexity of structure and variety of polymerization of the butadiene components which proceeding at interaction of cobalt and neodymium containing catalytic systems, have not allowed to approach to studying the nature of the active centers forming this or that type of parts, and finding out of the mechanism of stereoregulation till now. Besides the important place is given to consideration of reactions of transfer of a circuit on polymer and the cross growth, underlying the mechanism of branching of macromolecules of polymer. On the basis of the offered kinetic scheme mathematical modeling process, that together with a inverse problem of identification allows to come nearer to finding out of the true mechanism of polymerization and to define all basic rate constants of reactions of elementary stages of process, is carried out. Research of the hydrodynamics in reactors of the cascade is carried out, as a result of numerical experiments heterogeneity of fields of temperatures, speeds and concentration are revealed.

REVERSE FLOW REACTOR WITH FOAM CATALYSTS: EXPERIMENTAL STUDY AND PERFORMANCE COMPARISON

Marín P., Ordóñez S., Díez F.

Department of Chemical and Environmental Engineering. University of Oviedo.
Julián Clavería 8. E-33006 Oviedo. SPAIN, marinpablo@uniovi.es

Reverse flow reactors (RFRs) belong to the group of fixed-bed reactors operated under forced unsteady-state conditions, in this case achieved by periodically reversing the feed flow direction. One of the most studied applications of this reactor type is the catalytic combustion of gaseous lean emissions of hydrocarbons. The main advantage of using RFR technology is the high thermal efficiency, allowing autothermal operation with low temperature feeding and without auxiliary fuel, even for very lean hydrocarbon emissions (20-30°C of adiabatic temperature rise) [1, 2]. Initially, the reactor bed must be pre-heated above the ignition temperature of the hydrocarbon-air mixture. Then, the pre-heating is discontinued, the feed is introduced at room temperature, and the periodic switching of the flow direction started. The RFR principle is based on the difference of speed between a flowing gas and a temperature moving front travelling through the solid bed. Using an appropriate reversing switching time, part of the heat released by the exothermic reaction can be trapped inside the reactor in a half-cycle, being used to heat up the cold feed during the following half-cycle.

Traditionally, RFRs have been filled with particulate catalysts (spheres, extrudates, Raschig rings, etc) [1]. However, particulate beds present an important disadvantage when treating high flow rate gaseous emissions, i.e. the high pressure drop across the bed. For this reason, structured beds with low pressure drops, such as monoliths or foams, have been successfully used for other environmental catalytic applications (i.e. selective catalytic reduction of nitrogen oxides or automotive catalyst, among others) [3]. The main problem for extending these bed types to the RFR technology is the lower thermal inertia of the catalytic bed in comparison to particulate beds, resulting in a decrease of the reactor stability [4].

In the present work, the performance of a foam catalytic bed is studied experimentally in a bench-scale RFR for the combustion of lean methane-air mixtures. Foam supports balance of the advantages and disadvantages of particulate and monolithic bed types. Methane has been selected as model hydrocarbon, because it is difficult to oxidize by catalytic combustion (higher temperature and more active catalyst are required), so a good performance of the reactor can be easily extended to other compounds. The foam support consists in a reticulated structure of β-SiC, which generates a network of open interconnected cells and provides high external surface area with low pressure drops [5, 6]. The Pd active phase has been added by incipient wetness impregnation to the non-washcoated foam support, since it has appreciable porosity (25 m^2/g of BET surface area).

The reactor, a 0.8 m length 0.05 m internal diameter 316 stainless steel tube, houses three different beds: a catalytic one in the middle (0.250 m length), and two inert-ones (foam without active phase) at both sides (0.125 m length each). The experiments have been carried out under adiabatic conditions, as common in industrial-scale RFRs of large diameter, using a special oven equipped with a dynamic temperature control system. This unit, described in detail in previous works [7, 8], has been satisfactory tested, showing near-adiabatic operation. The most important RFR operating conditions have been studied: surface velocity, feed hydrocarbon concentration and switching time. The results have been compared to experimental data obtained in the same reactor for particulate and monolithic bed types. The comparison among the bed types must be done considering the differences in reactor stability, which are translated in higher or lower reactor lengths, catalyst cost and pressure drop.

References

[1] Matros, Y. S.; Bunimovich, G. A., Reverse-Flow Operation in Fixed Bed Catalytic Reactors. *Catalysis Reviews* **1996,** 38, (1), 1 - 68.

[2] Kolios, G.; Frauhammer, J.; Eigenberger, G., Autothermal fixed-bed reactor concepts. *Chemical Engineering Science* **2000,** 55, (24), 5945-5967.

[3] Cybulski, A.; Moulijn, J. A., *Structured Catalysts and Reactors*. 2nd ed.; Taylor & Francis Group: 2006.

[4] Marin, P.; Hevia, M. A. G.; Ordonez, S.; Diez, F. V., Combustion of methane lean mixtures in reverse flow reactors: Comparison between packed and structured catalyst beds. *Catalysis Today* **2005,** 105, (3-4), 701-708.

[5] Lacroix, M.; Nguyen, P.; Schweich, D.; Pham Huu, C.; Savin-Poncet, S.; Edouard, D., Pressure drop measurements and modeling on SiC foams. *Chemical Engineering Science* **2007,** 62, (12), 3259-3267.

[6] Twigg, M. V.; Richardson, J. T., Theory and Applications of Ceramic Foam Catalysts. *Chemical Engineering Research and Design* **2002,** 80, (2), 183-189.

[7] Fissore, D.; Barresi, A. A.; Baldi, G.; Hevia, M. A. G.; Ordóñez, S.; Díez, F. V., Design and testing of small-scale unsteady-state afterburners and reactors. *Aiche Journal* **2005,** 51, (6), 1654-1664.

[8] Marin, P.; Ordonez, S.; Diez, F. V., Combustion of toluene-hexane binary mixtures in a reverse flow catalytic reactor. *Chemical Engineering Science* **2008,** 63, (20), 5003-5009.

FLOW-RECIRCULATION METHOD FOR INVESTIGATION OF ALKYLATION OF BENZENE WITH ETHYLENE

Matrosova M.M., **Bobrov N.N.**, **Parmon V.N.**

Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
himitsu08@mail.ru

The alkilation of benzen with ethylene to ethylbenzene (EB) is important industrial process as EB is the key intermidiate in the manufacture of styrene. One problem in the manufacture of EB is undesirable by-products production. EB can later andergo other reactions producing mainly diethyl- and triethylbenzen, wich reduce the yeld of EB and affect the efficiency of the process. Another product formed in appreciable quantities, which reduces the EB quality, is xylene. Since separation of xylene from the EB product is very difficult, the production of xylene is very detrimental. Hence the understanding of the kinetics and alkilation mechanism could help in optimizing the reaction condition and desighn new catalyst for a more efficient process.

The reliable method for studying kinetiks and catalitic properties is flow-recirculation method (FRM), which allow one to generate ideal stirring conditions in a laboratory reactor [1]. Under these conditions, the catalyst bed is isothermal and the contact reaction mixture over the surface of all catalyst grains has practically the same composition. The FRM experimental techniques and devices for testing catalytic activity are developed in the Borescov Instutute of Catalysis SB RAS for more than 20 years and they were subsiquently improved in recent years [2].

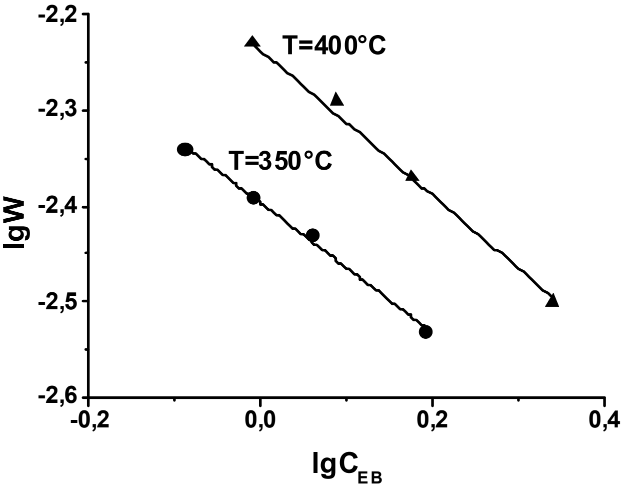


Fig. 1. The dependence of reaction rate on the temperature.

In this work we have for the first time applied the FRM for the investigation of alkilation of benzene with ethylene so as to obtain one-parameter dependences of the reaction rate on both the temperature and the concentrations of the reaction mixture components (Fig. 1), and the solution of inverse kinetic problem. It was shown that reaction kinetic is sensitive to EB concentration in the reaction mixture and the increase of EB concentration causes the reducing of reaction rate. It was found that the reaction rate dependence on temperature has a maximum near 400°C. The temperature dependence and the activation energy E_a=55.5 kJ/mol is in general agreement with data of literature.

References

[1]. Temkin M.I., Kiperman S.L., Lukiyanova L.I., *Dokl. Akad. Nauk SSSR*, **1950**, 94, 763–766.

[2]. Bobrov N.N., Parmon V.N., in *Principles and Methods for Accelerated Catalyst Design and Testing*, NATOScience Series II: Mathematics, Physics and Chemistry, Dordrecht: Kluwer, **2002**, 69, 197–215.

TO A PROBLEM OF OPTIMIZATION OF FUNCTIONAL MATERIALS TECHNOLOGY

Melikhov I.V., Rudin V.N., Severin A.V., Simonov E.F., Bozhevolnov V.E.

Chemical Department of Moscow State University, Moscow, Russia
helbyv@mail.ru

In connection with development of nanotechnology and nanomedicine problem of optimum technology of disperse materials with the properties most corresponding to conditions of their use became more actual. Usually optimum variant of technology is choosen on the basis of the physical and chemical data about the processes leading to a required material, but the data are accumulated fragmentary. For full optimization it is necessary to gather the information about functional $\vec{\Phi} = \vec{\Phi}\left\{\vec{Z}\left[\vec{X}\left(\vec{Y}[\vec{g}]\right)\right]\right\}$, where $\vec{\Phi}$ and $\vec{Z}$ – set of the properties characterizing a material in the conditions of use and on output of the reactor, $\vec{X}$ and $\vec{Y}$ – properties of substance particles and medium surrounding them in reactor volume, $\vec{g}$ – parameters characterizing a design and an operating mode of the reactor.

Functional $\vec{\Phi}$ assumes accumulation of the necessary information step by step:

1. Revealing $\vec{\Phi} = \left\{\Phi_1 \ldots \Phi_i \ldots \Phi_p\right\}$, where $\vec{\Phi}_i$ is functional property of substance (sorption ability, catalytic activity, speed of dissolution etc.) which is determined by observing behavior of trial material variants in the conditions of their use.
2. Determination of $\vec{\Phi}(\vec{Z})$ functions at $\vec{Z} = \left\{Z_1 \ldots Z_i \ldots Z_p\right\}$, where Z_i – physical and chemical property of substance, which can be varied in vitro; detection range of $\vec{Z}$ in which desired functional values are acceptable.
3. Obtaining of substance with different properties $\vec{X} = \left\{X_1 \ldots X_i\right\}$ of its particles at a laboratory variation of medium properties; determination of functions $\vec{Z}(\vec{X})$ and $\vec{X}(\vec{Y})$.
4. Studying the dependence of $\vec{Y}$ from $\vec{g}$ and a choice of a design and operating mode of reactor in which condition $\dfrac{d\vec{\Phi}/\vec{\Phi}_0}{dM/M_0} \rightarrow \max$ would be realized, where $\vec{\Phi}_0$ – the characteristics of a functional material similar before used, M_0 and M – weights of the substance introduced to reactor and product.

PP-I-37

Now boundary conditions to the listed stages are formulated. Their solution allow to optimize accumulation of the trial data about functional $\vec{\Phi}$ are formulated. Capability of such optimization was confirmed by working out of drugs for bone surgery and stomatology.

THE INFLUENCE OF REACTION MIXTURE ON ACTIVITY AND SELECTIVITY IN METHANOL SYNTHESIS REACTION

Mierczynski P., Maniecki T.P., Bawolak - Olczak K., Jozwiak W.K.

Technical University of Lodz Institute of General and Ecological Chemistry
Zeromskiego 116, 90-924, Lodz, Poland

Methanol is considered an alternative energy source, a medium for the storage and transportation of hydrogen and a starting feedstock for many chemicals as well. Commercially, methanol is produced from natural gas or coal via syngas, mainly containing CO and H_2 along with a small amount of CO_2, which has been developed by ICI, Lurgi, Topsoe and MGC etc. over the last century. The potential use of CO_2, the most important greenhouse gas, as an alternative feedstock replacing CO in the methanol production has received attention as an effective way of CO_2 utilization [1, 2].

The comparative studies of physicochemical properties and catalytic activity for copper catalysts supported on different support were the main goal of this work. Catalysts were prepared by wet aqueous impregnation. To prepare the precursor of support nitrates of Al, Fe, Cr and $Zn(CH_3COO)_2 \cdot 3H_2O$ were used. The ammonia co - precipitated mixture of appreciate hydroxides contains the metal in corresponding molar ratio: Al/Cr=3, Al/Fe=1 and Al/Zn=2 were dried and calcined. Metal phase were impregnated on supports and then the supported catalysts were dried and finally calcined in the same conditions in the air at 400°C for 4h. The physicochemical properties of the support and supported copper catalysts were determined by BET, XRD, TPR-H_2, and CO_2 -TPD. The activity tests in methanol synthesis were carried out under elevated pressure (4MPa) at 180°C and 260°C from CO - H_2 or CO - H_2 mixture with GC and Ms analysis.

The comparative studies carried out for catalytic systems show that :

- Introduction second ions into alumina decrease specific surface area.
- Addition of cooper shifts the reduction effects toward lower temperature.
- The formation of spinel structure $ZnAl_2O_4$ and binary oxide $CrAl_3O_6$ and $FeAlO_3$ during calcinations process was confirmed by XRD technique for appreciate support.
- The formation of copper chromate and copper aluminates during calcinations process was proved.
- Activity tests show that the most promising system for methanol synthesis were $Cu/ZnAl_2O_4$ and $Cu/CrAl_3O_6$ catalysts.

- Catalytic tests showed that yields and selectivity of methanol synthesis depends strongly on the kind of support (see table 1).

Table 1. Yield of methanol and selectivity in methanol synthesis from CO - H_2 and CO_2 - H_2 mixture for copper supported catalyst.

Catalyst	Hydrogenation of CO						
	Yield [g CH_3OH/kg $_{cat.}$ h^{-1}]	Selectivity at 260°C					
		CH_4	CH_3OH	C_2H_5OH	C_3H_7OH	HCOH	Other
20%Cu/$CrAl_3O_6$	108	6%	90%	1%	1%	2%	-
20%Cu/$ZnAl_2O_4$	50	5%	92%	1%	1%	1%	-
20%Cu/$FeAlO_3$	232	24%	29%	11%	13%	18%	5%
Catalyst	Hydrogenation of CO_2						
	Yield [g CH_3OH/kg $_{cat.}$ h^{-1}]	Selectivity at 260°C					
		CH_4	CH_3OH	C_2H_5OH	C_3H_7OH	HCOH	Other
20%Cu/$CrAl_3O_6$	75	-	81%	10%	-	-	9%
20%Cu/$ZnAl_2O_4$	252	-	95%	1%	-	-	4%
20%Cu/$FeAlO_3$	110	25%	33%	12%	9%	21%	-

References:

[1]. Chinchen, G.C., Mansfield, M.S., CHEMTECH Nov, **1990**, 692.

[2]. Inui T., Hara H., Takeguchi M., and Kim J.B., Catal. Today **1997**, 36**,** 25.

The partial financial support of this work by the Polish Scientific Research Council supports (Grant No. N N209 011234) is gratefully acknowledged

METHANOL OXIDATIVE STEAM REFORMING FOR HYDROGEN PRODUCTION OVER Cu – Au / $ZnAl_2O_4$ CATALYSTS

Mierczynski P., Maniecki T.P., Rynkowski J.M., Bawola-Olczak K., Jozwiak W.K.

Technical University of Lodz Institute of General and Ecological Chemistry
Zeromskiego 116, 90-924, Lodz, Poland

Hydrogen production is one of the most important raw material for ammonia synthesis, synthetic gasoline production and many others. During last years hydrogen was successfully applied as a fuel for fuel cells used in mobile devices (mobile phones, laptops etc). Industrially hydrogen is produced via gasification of biomass or natural oil. Unfortunately such processes cannot be applied in small mobile devices. An interesting opportunity seems to be oxidative methanol reforming (OSR). Those reactions took place in temperature range (150-350°C) and under atmospheric pressure.

$$CH_3OH + 0{,}5O_2 \rightarrow CO_2 + 2H_2 \qquad \Delta H = -192{,}2\ KJ/mol \qquad (1)$$

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2 \qquad \Delta H = 49{,}7\ KJ/mol \qquad (2)$$

Combination of both reactions (1 and 2) allows to run this reaction as autothermal process.

$$CH_3OH + 0{,}25\ O_2 + 0{,}5\ H_2O \rightarrow CO_2 + 2{,}5\ H_2\ \Delta H = -71{,}4\ KJ/mol \qquad (3)$$

The mail goal of this work was the determination of the influence of copper loading and gold promotion on catalytic activity and selectivity of Au - Cu / $ZnAl_2O_4$ supported catalysts in OSR of methanol.

The catalysts were prepared by impregnation method, the meal loading was 5 - $60\%_{wt}$ of Cu and 1 - 5% of Au, respectively. Methanol mixed reforming starts at 170°C and reaches 100% of CH_3OH above 300 °C. Selectivity to CO_2 and H_2 was close to 100%, only CO as a side product was detected. Copper loading has strong influence on methanol conversion degree. The optimum copper content was 20%, such systems reveal highest activity.

Gold promotion has no strong influence on the catalytic activity but improve selectivity to H_2 and CO_2 products.

PP-I-40

PACKED ABSORBER FOR THE ISOLATION OF L-LACTIDE

Mulyashov S.A.[1], **Sirovski F.S.**[2], **Grechishkina O.S.**[3] **and Kolbakov V.V.**[4]

[3]*D.I. Mendeleev Univercity of Chemical Technology of Russia, Moscow, Russia,*
e-mail: olgrech@ hotmail.com
[1,2,4]*OU Nordbiochem, Estonia, e-mail: vambola@nordbiochtm.com*

The production of biodegradable polymers is based on polylactic acid (PLA). This acid is produced by polymerisation of a cyclic dimer that in turn is obtained from microbial L-acid. The known process of PLA manufacture comprises the synthesis of an oligomer with molecular mass around 1000-5000 Daltons with its subsequent depolymerisation. This reaction is carried out at 190-220 °C and residual pressure 10-15 mm Hg giving also the considerable amount of side-products. The partial yield of the desired product (L-lactide) could be increased by dropping the depolymerisation temperature and respectively reaction pressure to 1-3 mm Hg. Unfortunately, under these conditions the complete removal of L-lactide with m.p. 97 °C out of the gas phase becomes virtually impossible. The traces of L-lactide are found all along the vacuum line as well as in the vacuum pumps themselves and the equipment operation is seriously compromised. The issue could be solved using packed absorbers.

We have run several simulations of the packed absorber operation using ChemCad software. The plant included the depolymerisation reactor (a 70 l volume stirred jacketed tank) and the packed absorber installed on the vacuum line. The reactor temperature was maintained in the range 160-260 °C. The regimes of the reactor and absorber operations were synchronised. It was shown that washing by aromatic solvents ensures virtually complete removal of L-lactide from the gas phase.

CORRECT INVESTIGATION OF THE CATALYTIC ACTIVITY AND SIZE EFFECT IN METHANE OXIDATION OVER Pt/γ-Al_2O_3 CATALYSTS

Ilya Yu. Pakharukov[1,2], **Irene E. Beck**[1,2], **Valerii I. Bukhtiyarov**[1,2],
Vladimir I. Zaikovsky[1], **Vladimir V. Kriventsov**[1], **Valentin N. Parmon**[1,2]

[1]*Boreskov Institute of Catalysis SB RAS, pr. Lavrentieva 5, Novosibirsk, 630090, Russia, E-mail: ilyapakharukov@yandex.ru*
[2]*Novosibirsk State University, str. Pirogova 2, Novosibirsk, 630090, Russia*

Methane catalytic deep oxidation attracts great attention due to economic and ecological reasons. This process is essential in pollution control for both stationary and mobile applications. Moreover the catalytic combustion of methane has been extensively studied as an alternative to conventional thermal combustion.

Structure sensitivity of certain types of reactions on supported metal catalysts is of great interest in heterogeneous catalysis. The data about structural sensitivity of considered oxidation processes on Pt – containing catalysts are still controversial in the literature. Usually the catalytic activity is evaluated by conversion normalized to quantitative catalyst characteristic such as weight, number of active sites etc. However this approach is inaccurate because of absence of proportionality between these values. The specific reaction rate depends on temperature and component concentrations only, so it can be used as accurate measure of catalytic activity. The turnover frequency (TOF) changing as a function of particle size of active component is main criterion of structure sensitivity of reactions. Reaction rate measurements carried out under differential conditions are most precise. The flow- recirculation method allows to achieve the gradientless mode in laboratory reactor [1].

In this work, the sensitivity of methane oxidation turnover frequencies to Pt average particle size was studied over two series 0.7 wt.% Pt/γ-Al_2O_3 catalysts. Our goal was to obtain more information on the structure sensitivity of this process by means of the modern flow-recirculation method.

Transmission electron microscopy was used to characterize the Pt average particle size and dispersion. XAFS spectroscopy was used to study oxidation state of the supported Pt species.

The correct comparison of catalytic activities allowed to detect considerable impact of the Pt nanoparticle size on the TOF value. Data illustrating size sensitivity of methane deep oxidation are shown in Figure 1.

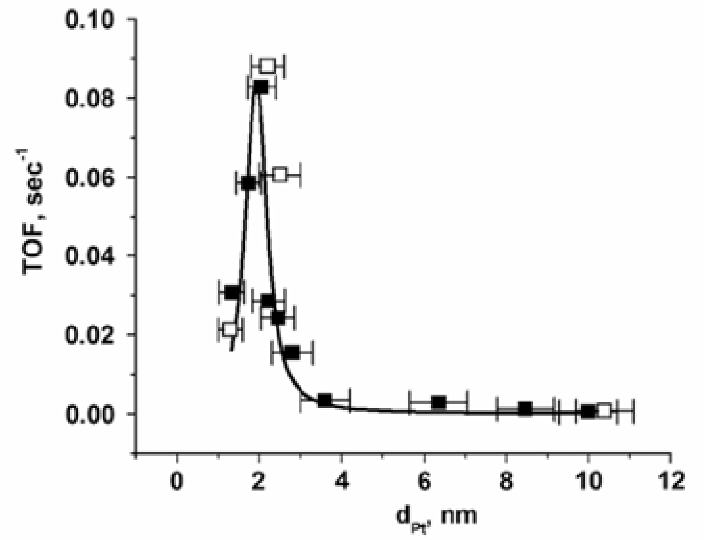


Figure 1. Turnover frequencies in the CH_4 oxidation at 700 K as a function of the mean size of the Pt particles supported on γ-Al_2O_3. The black and open squares correspond to the samples of first and second series.

In order to explain observed size effect an idea of possible thermodynamic influence of the particle size on the catalytic reaction rate and apparent activation energy [2] was considered and modeling was performed. This thermodynamic approach describes only TOF growth with decrease in particle size from 10 to 2 nm and the size dependence of the apparent activation energy of the process, but not further TOF reduction for the catalysts with d(Pt) < 2 nm. The most probable explanation of this disagreement is change of reaction mechanisms or different chemical state of active component. Indeed, the XAFS data revealed the change of Pt oxidation state at nanoparticle sizes below 2 nm. The observed decrease in the TOF value at diminishing Pt nanoparticle sizes below 2 nm seems to be due to predominantly non-metallic nature of so fine platinum particles because of a strong interaction with the support.

References

[1]. N.N. Bobrov, V.N. Parmon, in: NATO Science Series II: Mathematics, Physics and Chemistry, vol. 69, Kluwer, **2002**, p. 197.

[2]. V.N. Parmon, Dokl. Phys. Chem. Vol. 413, **2007**, p. 42.

[3]. I.E. Beck, V.I. Bukhtiyarov, I.Yu. Pakharukov, V.I. Zaikovsky, V.V. Kriventsov, V.N. Parmon Journal of Catalysis Vol. 268, **2009**, p. 60.

Acknowledgements

We are grateful to theFederal Education Agency for financial support within governmentcontract №P252/23.07.2009.

NEW APPROACH OF DEFINITION OF NUMBER OF STATIONARY STATES FOR CATALYTIC REACTIONS

Patmar E.S., **Koltsov N.I.**

Chuvash State University, Cheboksary, Russia
E-mail: edi75@mail.ru, koltsovni@mail.ru

One of stages of the decision of a return problem of chemical kinetics is discrimination of mechanisms of reactions on number of internal stationary states (ISS) - stationary states in which concentration of all intermediate substances nonzero. In work [1] the criterion of multiplicity of stationary states has been developed. This criterion allows to hold on discrimination of mechanisms on the basis of a realization two ISS. However this method does not give an opportunity to determine a realization of three and more ISS. In [2] is shown that ISS number can grow wrilimited all bounds with growth intermediate substances number. In [3] the possibility of exponentional increases in ISS number with growth of quantity of intermediate substances is established: for the mechanisms with three intermediate substances probably up to 9 ISS, for the mechanisms with four intermediate substances – 27 ISS's and in general for mechanisms with n intermediate substances are possible 3^{n-1} ISS. We develop the new approach for definition of number ISS for one-route catalytic reactions. It consists in the following:

1) from investigated set of equations stationary expressions for constants of stage rates are defined;
2) the set of all possible values of concentration of intermediate substances breaks on n-dimensional (as a rule rectangular) areas;
3) for each of these areas possible values of constants of stage rates (area of values of constants) are counted up;
4) maximum number ISS from a condition is defined that it does not surpass number of areas of concentration of intermediate substances for which values of stage rates constants can be identical.

The resulted approach allows not only to position a realizability of certain number ISS but also and to construct the areas characterised by set number ISS. Therefore it is applicable both at discrimination of mechanisms and for a finding of conditions at which concrete number ISS for investigated reaction is realised.

For the reaction

$$2CO + O_2 \rightarrow 2CO_2, \tag{1}$$

proceeding via the stage scheme:

$$\begin{aligned}
&1.\ CO + K \Leftrightarrow KCO,\\
&2.\ 2K + O_2 \Rightarrow 2KO,\\
&3.\ KCO + KO \Rightarrow KCO_2 + K,\\
&4.\ 3KCO_2 \Leftrightarrow 2KCO_2 + K + CO_2,\\
&5.\ KCO_2 \Rightarrow K + CO_2.
\end{aligned} \tag{2}$$

With use described above the approach possibility of existence of six ISS has been positioned (fig. 1).

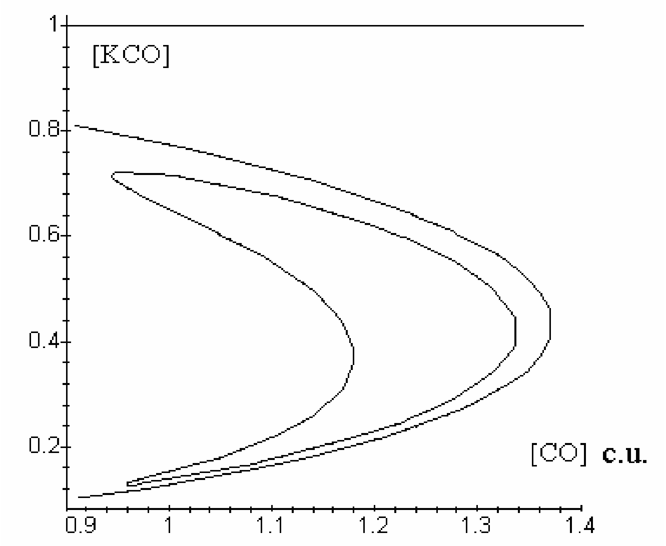


Fig. 1. Dependences of concentration of intermediate substance KCO from concentration CO for the reaction (1) proceeding via schema (2) at: k_1=1; k_{-1}=10^{-3}; k_2=5; k_3=101; k_4=35,5∙10^3; k_{-4}=2,5∙10^4; k_5=125 (s^{-1})

Thus the stated approach allows to define number of internal stationary states of the one-route catalytic reactions proceeding on multistage nonlinear mechanisms. This approach gives the chance to choose for investigated reaction from several prospective mechanisms the certain mechanism characterised set positioned experimentally number of nonzero stationary states.

References

[1]. Koltsov N.I., Fedotov V.Kh., Alexeev B.V. // Repors of AN SSSR. 1988. V. 302. N1. P.126.
[2]. Alexeev B.V., Koltsov N.I. // Mendeleev Communications. 1998. V.8. №3. P.116.
[3]. Patmar E.S., Alexeev B.V., Koltsov N.I. Repors of AN SSSR. 2000. V.371. N5. P. 638.

STREAM HEAT EXCHANGE OF AEROSOLS IN A TUBULAR REACTOR

Pechenegov J.Y.[1], **Kuzmina R.I.**[2], **Kosova O.J.**[1]

[1]Saratov state technical university,
Russia, 413100, the city of Engels, Freedom area, 17, E-mail: mxp@techn.sstu.ru
[2]The Saratov state university of a name of N.G. Chernyshevskogo, Russia, 410012,
the city of Saratov, street Astrakhan, 83, E-mail: Kuzminaraisa@mail.ru

In work the mathematical model and algorithm of calculation of heat change of a current aerosols in the tubular reactor, giving comprehensible result ins on accuracy enough wide spacings of variation of influencing arguments is introduced.

At compiling of mathematical model following physical submissions and assumptions were used.

1. Presence of fragments in a gas current does not inflect a field of speeds and turbulent pattern of a carrying agent.

2. Thermal interaction of particles is carried out only with a gas phase.

3. On spacing interval from a wall in the range from 0 to $d_t/2$ (field of a viscous intermediate layer) gravity of a heat flow $q_{\text{р}}=\lambda_{\text{ст}}\,\mathrm{d}t/\mathrm{d}y$ keeps the constant value equal to value of gravity of a heat flow $q_{\text{п, ст}}$ on a wall. At $y=d_{t/2\div r}$ complementary to the molecular dodge of carrying of heat in a gas phase there is a turbulent carrying with gravity of a heat flow $q_{\text{п, тб}} = \lambda_{\text{тб}}/\mathrm{d}y$ and carrying of heat with radially migrating firm fragments $q_{\text{п, т}}=\lambda_{\text{п, т}}\,\mathrm{d}t_t/\mathrm{d}y$. Resultant gravity of a heat flow $q_{\text{п}} =(\lambda+\lambda_{\text{тб}})\,\mathrm{d}t_g/\mathrm{d}y+\lambda_{\text{п, т}}\,\mathrm{d}t_t/\mathrm{d}y$ in a radial direction for a spacing *at* from $d_t/2$ to R is inflected linearly according to expression $q_{\text{п}} = q_{\text{п, ст}}\,[1\,(y-0{,}5\,d_{\text{т}})\,/\,(R-0{,}5\,d_{\text{т}})]$.

4. At calculus of coefficients of turbulent thermal conductivity $\lambda_{\text{тб}}$ and seeming thermal conductivity of a current of firm fragments $\lambda_{\text{п, т}}$ connections for turbulent Prandtl number are used $Pr_{\text{тб}} = 0{,}9 + 182{,}4\,/\,(Pr\cdot Re^{0{,}888})$ and the factor of high-speed slip of fragments $\frac{\varphi}{\upsilon}=1\Big/\left[1+c^{*}\left(\frac{\rho_m}{\rho}-1\right)^{2/3}\left(\frac{d_m}{D}\right)^{2/3}\left(1+\frac{200}{Fr-Fr_{\text{вз}}}\right)\right]$, where c^{*} - the skilled coefficient, is equal $c^{*} = 0{,}0565 - 0{,}003K$; Fr and $Fr_{\text{вз}}$ – Frud numbers determined on speed of gas and speed of weighing of fragments accordingly.

The field of a current of a current is conditionally broken down on n elementary concentric strata. Thickness maiden (near a wall) a stratum $y_1 = 0,5\ (\Delta y + d_т)$, and the subsequent strata – $\Delta y = (R – 0,5\ d_т) / (n – 0,5)$.

In a current direction the calculated schema envisions current breakdown by diametrical sections, on spacing interval Δx from each other.

The algorithm of calculation of heat change and indispensable length of a tube for heating of a current to the set temperature $t_п$ at the set allocation of temperature of a wall $t_{ст} = t_{ст}\ (x)$ includes calculus of domestic gravity of a heat flow $q''_{п,ст}$, temperature allocations $t_{в,\ i}$ in a radial direction and mean values of temperatures of phases $t''_{г,ср}$ and $t''_{т,ср}$ in diametrical section of an exit of each of succession of leases Δx_j.

On fig. 1 calculation on the designed algorithm is compared to data of different authors for chemically inert aerosols in co-ordinates $Q_n/Q = f\ (x/D)$. Magnitudes transmitted from a pipe wall to a current aerosols (or on the contrary) calorific powers Q_n are determined by calculation on the private skilled equations received by explorers. Calorific power Q corresponds to a current of gas without fragments. From fig. 1 it is visible, that results of calculation will well be matched test data available in the literature.

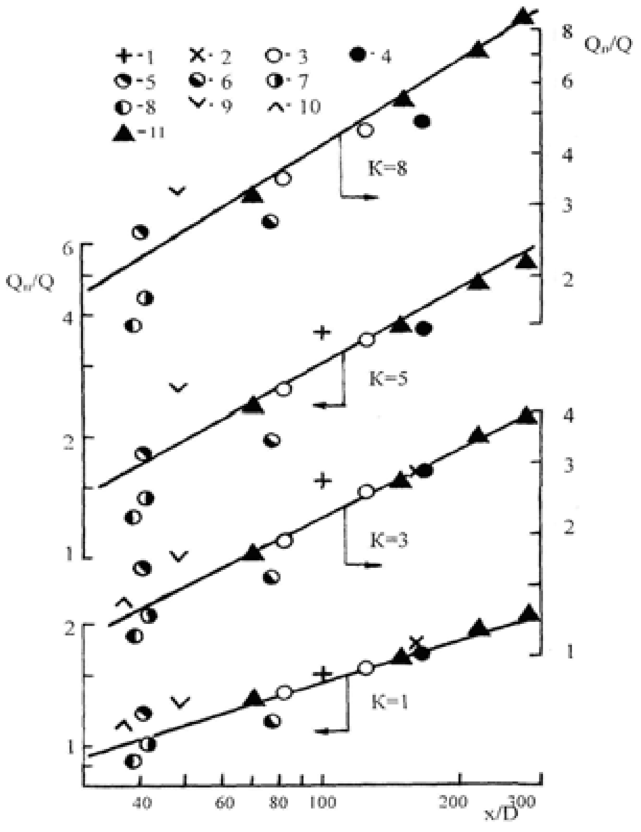


Fig. 1. Dependence Q_n/Q from x/D: lines – our calculation on tendered algorithm (Re=10^4; t_{CT}=100 °C; current temperature on an input t_o=0 °C); 1÷11 – calculation with use of skilled formulas of different authors (diameter of tubes D = 8 ÷ 50 mm, the sizes of fragments d_T = 3 ÷ 865 microns)

Comparison of results of calculation with our experimental data on heat change of a current of air with decaying fragments of bicarbonate of sodium (Furnacing reaction) also has demonstrated on quite satisfactory convergence calculated and test data.

HIGH TEMPERATURE OXYGEN TRANSPORT IN MIXED OXIDES WITH STRUCTURE OF FLUORITE AND PEROVSKITE. EFFECT OF OXYGEN MOBILITY ON CATALYTIC PROPERTIES IN THE REACTIONS WITH OXYGEN PARTICIPATION

Pinaeva L.G., Sadovskaya E.M., Ivanov D.V., Isupova L.A.

Boreskov Institute of Catalysis SB RAS, pr. Lavrentieva, 5, 630090, Novosibirsk, Russia, e-mail: pinaeva@catalysis.ru

Mixed oxides with structure of fluorite or perovskite constitute a broad class of the catalysts for high temperature processes with oxygen participation. It is commonly considered that their activity in the reactions of hydrocarbons oxidation is due to high lattice oxygen mobility. Nevertheless, until now no direct correlation between the reaction rate and the coefficient of oxygen diffusion as measured in the close conditions was reported. As to other reactions, the nature of the factors determining their activity is still open. Present study was focused on elucidation of the mechanism of oxygen transport in the La-Sr-(Mn,Fe)-O and Ce-Zr-(La)O mixed oxides and possible relationships between oxygen mobility and catalytic activity in the reactions of methane and ammonia oxidation, nitrous oxide decomposition and CO water gas shift.

Transient experiments on the interaction of the reaction mixture with the catalysts unambiguously showed that it is the lattice oxygen that is included into reaction products at methane oxidation and CO water gas shift. The same conclusion for the reaction of N_2O decomposition followed from the dynamics of labeled oxygen (^{18}O) transfer from the catalyst to gas phase products.

Investigation of the kinetics of isotope exchange between $^{18}O_2$ and mixed oxides in the temperature range 600÷900°C showed that the sharp increase of both the rate of oxygen exchange on the surface and the oxygen diffusion in the bulk can be due to appearance of fast pathway of oxygen transfer through defects (Fig.1). For perovskites, these defects include both isolated and ordered in the lanthanide planes oxygen vacancies that are formed in the lattice to compensate the reduced cation charge at Sr substitution for La. Developed network of domain boundaries determines high rate of oxygen exchange in the fluorites. Supporting of Pt clusters additionally increases the oxygen mobility due to fast oxygen transfer from Pt to support (characteristic time < 10^{-2} s) and formation of oxygen vacancies originated from the incorporation of highly dispersed Pt atoms into the mixed oxide lattice through the domain boundaries.

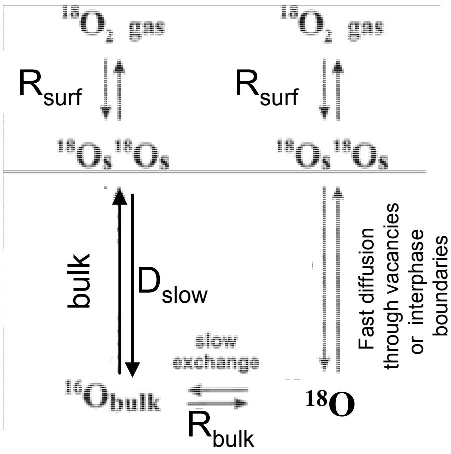


Fig. 1. Scheme of gas / surface (subsurface) /bulk oxygen exchange in themixed oxides.

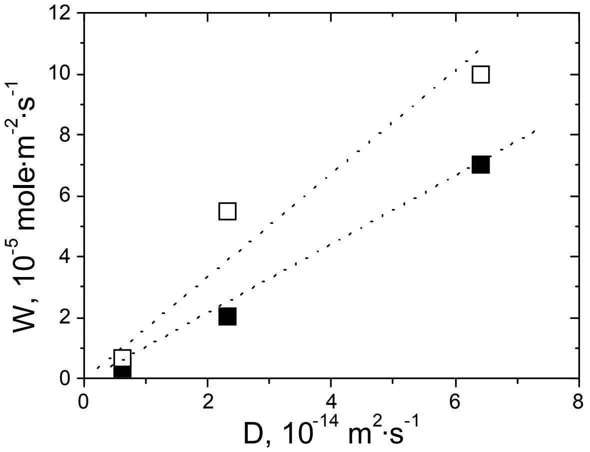


Fig. 2. The specific catalytic activity with regard to CH_4 combustion (□) or N_2O decomposition (■) versus coefficient of oxygen diffusion dependence for La-Sr-Mn-O mixed oxides. T = 900°C.

All intrinsic kinetic parameters related to oxygen activation and diffusion both in the mixed oxides and in the metal – mixed oxide systems were calculated by the numerical analysis of experimental curves in accordance with proposed models.

The obvious correlation between the coefficient of oxygen diffusion in perovskite or fluorite based catalysts and their specific activity in a large number of reactions with participation of oxygen was found. Fig.2 shows the examples of such correlation for the catalytic systems “perovskite - methane oxidation” and “perovskite – N_2O decomposition”.

Performed study shows a decisive role of lattice oxygen mobility in the high temperature catalytic activity of mixed oxides in the reaction with oxygen participation.

KINETICS OF TRANSESTERIFICATION OF MICROALGAE OIL FOR THIRD GENERATION BIOFUELS PRODUCTION

Plata V.[1], **Kafarov V.**[1], **Moreno N.**[2]

[1]Industrial University of Santander, Department of Chemical Engineering, Carrera 27 calle 9, Bucaramanga, Colombia, tel. +57 +76344000 ext 2603, kafarov@uis.edu.co
[2]Colombian Petroleum Institute – ICP, Piedecuesta, Colombia

Exists now a strong worldwide trend towards the development of a type of so-called third generation biofuels, which are obtained by similar production methods to those used in the development of first and second generation biofuels, but applied to bioenergy crops specifically designed or adapted to enhance the conversion of biomass to biofuel. Among these, stands out the growing of different species of microalgae, whose oil can be used as feedstock in biodiesel production.

Transesterification is the commonly reaction used to produce biodiesel from an oil with an alcohol in the presence of a catalyst. The corresponding products are a mixture of fatty acid alkyl esters and glycerol. This reaction is sensitive to some parameters; the most important are reaction temperature, molar ratio of alcohol to oil and amount of catalyst, which have to be within a certain range of operation in order to ensure a high conversion.

A study of the kinetics of transesterification will provide parameters that can be used to predict the extent of the reaction at any time under particular conditions. Three consecutive and reversible reactions are believed to occur. Mono and diglycerides are the intermediates formed while three ester molecules are produced. Different authors have raised different reaction mechanisms for the transesterification of seed oil, which include pseudo second-order and second-order mechanism. Among several studies published on transesterification of microalgae oil, none are concerned about the reaction kinetics.

In this paper, transesterification of microalgae oil in the presence of NaOH as a catalist was conducted in a bacth reactor. The effect of the reaction temperature, molar ratio of alcohol to oil and amount of catalyst on rate constants and kinetic order were examined. Samples were collected during the reaction and analyzed by gas chromatography/flame ionization detector (GC/FID). The experimental mole concentrations were fitted to a mathematical model of a second-order kinetics without shunt reaction. The reaction rate constants were determined.

PP-I-45

This work was sponsored in the framework of projects supported by the Ministry of Agriculture and Rural Development and the Ibero-American Program on Science and Technology for Development (CYTED) project 306RTO279 “New technologies for biofuels production” UNESCO codes 330303, 332205,530603,330999 in conjunction with the Colombian Institute of Petroleum (ICP-ECOPETROL).

MATHEMATICAL MODELING AND OPTIMIZATION OF THE OXIDATIVE COUPLING OF METHANE OVER OXIDE-SILICON COMPOSITES

Podlesnaya M.V., **Zyskin A.G.**, **Makhlin V.A.**

A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, Russia

For almost three decades, the reaction of the oxidative coupling of methane has been attracting the attention of researches as a promising method for one-stage ethylene production from natural gas. Numerous studies devoted to searching of effective catalysts and kinetic studying in different countries are undertaken worldwide. Currently the catalytic systems on the basis of silicon composites containing manganese and tungsten oxides and alkali metals (Li, K, Na) attract the greatest interest [1-4]. It should be noted at the present time the reaction mechanism is incompletely studied. At the same time it is known that the reaction doesn't proceed selectively and along with main products – ethylene and ethane, there are carbon monoxide and dioxide and a little amount of hydrogen that are formed.

In present work mathematical modeling of kinetic study results of different authors [2, 5] is performed, and phenomenological reaction models differing in ethylene formation route are considered. Influence of process parameters (temperature, pressure, gas composition) over process performance is investigated. Optimum conditions for maximum ethylene or C_2 selectivity are determined. Keeping in mind the prospect of the industrial implementation of the process the theoretical basics of design are developed.

References

[1]. G. D. Nipan, A. G. Dedov, A. S. Loktev, V. A. Ketsko, T. N. Koltsova, A. A. Tyunjaev, I. I. Moiseev. // Doclady Physical Chemistry, 2008, Vol. 419, No. 5, 646.

[2]. Seyed Mehdi Kamali Shahri, Seyed Mehdi Alavi. // Journal of Natural Gas Chemistry, 2009, Vol. 18, 25–34.

[3]. Shengfu Ji, Tiancun Xiao, Shuben Li, Lingjun Chou, Bing Zhang, Chuanzhi Xu, Ruiling Hou, Andrew P.E. York, and Malcolm L.H. Green. // Journal of Catalysis, 2003, Vol. 220, 47–56.

[4]. Lingjun Chou, Yingchun Cai, Bing Zhang, Jianzhong Niu, Shengfu Ji and Shuben Li. // React. Kinet. Catal. Lett., 2002, Vol. 76, No. 2, 311-315.

[5]. A. G. Dedov, V. A. Makhlin, M. V. Podlesnaya, A. G. Zyskin, A. S. Loktev, A. A. Tyunjaev, G. D. Nipan, T. N. Koltsova, V. A. Ketsko, M. N. Kartasheva, and I. I. Moiseev. // Teoreticheskie Osnovy Khimicheskoi Tekhnologii, 2010, Vol. 44, No. 1, 3-13.

MATHEMATICAL MODELLING OF PROCESS OF METHANOL SYNTHESIS WITH THE SURFACE MECHANISM OF REACTIONS TAKEN INTO ACCOUNT

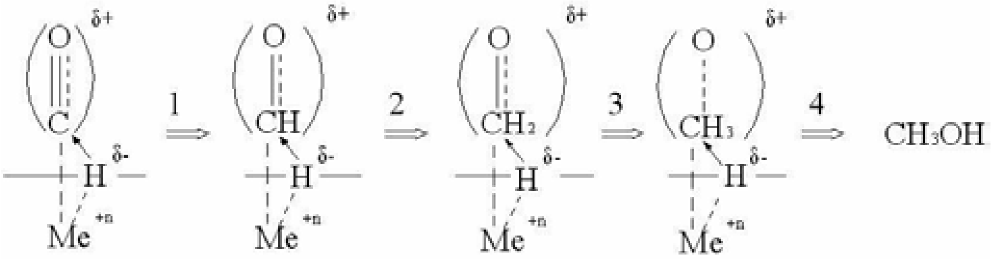
Popok E.V., Kravtsov A.V., Youriev E.M.

Tomsk Polytechnic University, Tomsk, Russia. E-mail: evgen-san@inbox.ru

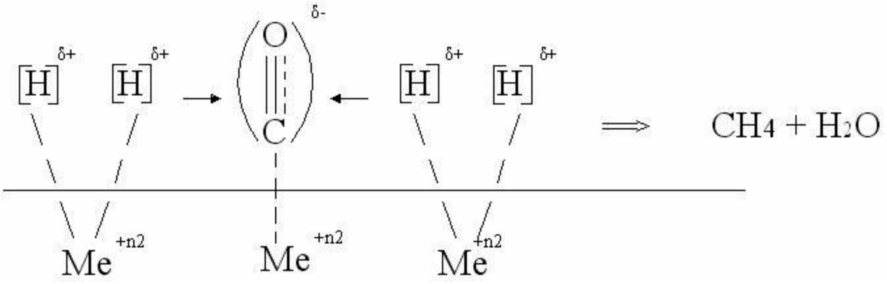
Cost of the basic industrial catalysts of methanol synthesis is high, therefore testing and a choice a catalytic system is the determinative factor for effective operation of process, especially for low-temperature synthesis on Zn-Cu-Al-contact system [1].

The old catalysts of methanol synthesis containing Zn and Cr. The condition of a surface of the catalyst with a low degree of restoration provided stability there catalytic systems and their high selectivity at insignificant speeds of course of the key reaction. When converting the process to using highly-active Zn-Cu-Al-catalytic systems here is a decrease a selectivity on reaction of methanol synthesis. Consequently there is a necessity of its preservation and creation of conditions on inhibition of collateral reaction of synthesis of hydrocarbons on Fisher-Tropsh reaction to the metal centers of the catalyst. This centers formed in conditions of thermal disintegration of Zn-Cu-clusters. The description of this process with using a method of mathematical modelling allows considering the mechanism of formation of the active center on a surface of the Zn-Cu-Al-catalyst, to define conditions of formation nanodispersed surfaces, modes of activation of cluster [2]. This method allows also resolve a problem of testing of catalysts of various marks of catalysts of methanol synthesis.

There are some conceptions about the mechanism of methanol synthesis on Zn-Cu-Al-catalysts. Authors of works [3, 4] as the most exact and proved was chosen the mechanism with formation positive charged chemisorbed complex on a surface weakly reduced catalyst and dissolution of hydrogen in near-surface layer of catalytic system. During consecutive stages (1-4) there is a saturation of chemical bond Me–CO by active hydrogen and detachment of an end-product – methanol.



The basic side reaction is reception of methane on Fisher-Tropsh reaction on metal centers of the Zn-Cu-Al-catalyst dynamically arising while in service:



Other collateral reactions, such as production of dimethyl ether and heavy spirits, are also considered in mathematical model, though amount of products of these reactions is low.

The purpose of this work was creation of adequate mathematical model of methanol synthesis, the considering mechanism of course of reactions on surfaces of the catalyst and the main diffusion resistance. Creation of model has been divided into four stages – by numbers of shelves in a reactor – in view of greater deactivation of the catalyst on the first shelf.

This mathematical model allows to accurately predict activity and selectivity of the catalyst during its operation, to select optimum modes for the most effective and long operation of the catalyst. It also allows to select for any plant of methanol synthesis the most suitable catalysts of various manufacturers providing a high yield of an end-product. As a result a selection of the optimum catalyst and a mode of its operation will lead to more effective work of installation and to reduction of the cost price of methanol.

References

[1]. Karpov S.A., Kunashev L.H, Mortikov E.S., Kapustin V.M. Production of methanol: current status of the industry and the tendency of development // Refining and petrochemistry.– **2009** . – №7. – p. 3 – 8.

[2]. Plyasova L.M., Yourieva T.M., Kriger T.A., Makarova O.V., Zaykovsky V.I., Soloveva L.P., Shmakov A.N. Formation of the catalyst of methanol synthesis // Kinetics and catalysis.– **1995**. – №3. – p. 464 – 472.

[3]. Kravtsov A.V. About dynamic features of the mechanism of reaction of hydrogenation carbon oxide // Questions of kinetics and catalysis. Intercollegiate collector articles. – Ivanovo: – **1980**. – p. 33 – 40.

[4]. Hye-Won Lim, Myung-June Park, Suk-Hwan Kang, Ho-Jeong Chae, Jong Wook Bae, Ki-Won Jun // Modeling of the Kinetics for Methanol Synthesis using Cu/ZnO/Al_2O_3/ZrO_2 Catalyst: Influence of Carbon Dioxide during Hydrogenation. Ind. Eng. Chem. Res. – 2009. – №48 (23), pp 10448–10455.

PP-I-48

CFD SIMULATION OF AN ABSORPTION COLUMN FOR A CO_2 CAPTURING PROCESS

Premalatha M., Kumar G.

Centre for Energy and Environmental Science and Technology, Department of Chemical Engineering, National Institute of Technology, Tiruchirappalli -620015, Tamil Nadu, India

Reduction of greenhouse gases is an important mitigation effort in the midst of rising global temperatures. This report is focused on the capture of CO_2 from flue gas emitted by a coal fired power plant. From available technologies, post combustion capture with chemical absorption is chosen, because this technology looks to be ready for retrofitting in the power plant. This approach is made towards the simulation of the process using computational fluid dynamic software. The CFD software used is FLUENT 6.3.26.

The absorption column is designed in GAMBIT by taking the dimensions of 8m height and 1m diameter of packing column and is exported to the FLUENT. In FLUENT, by specifying boundary and operating conditions (temperature, pressure, fluid flow models, flow rates, and porosity, iterations are done till the all the equations converge. Also, simulations were carried out for various porosities, liquid flow rates and gas flow rates to study the effect of CO_2 recovery. The variation in exit CO_2 concentration with respect to the operating conditions are examined and optimized. The simulated column showed CO_2 recovery of about 90% for a porosity=0.6, liquid flow rate 3.2kg/s and gas flow rate 1kg/s.

Key words: CO_2, absorption column, post combustion, FLUENT, porosity

EXPERIMENTAL STUDY OF THE HALIDE-FREE CARBONYLATION OF DIMETHYL ETHER TO METHYL ACETATE ON BIFUNCTIONAL $Rh/Cs_{1.5}H_{1.5}PW_{12}O_{40}$ CATALYST

Reshetnikov S.I., Izvekova A.A., Volkova G.G.

Boreskov Institute of Catalysis SB RAS, Pr. Akademika Lavrentieva 5,
Novosibirsk, 630090, Russia, E-mail: ggvolkova@catalysis.ru

Acetic acid is an important industrial chemical which is manufactured on a large scale. The main route to acetic acid is through the carbonylation of methanol in the Monsanto process which uses a homogeneous rhodium catalyst and halide promoter. Main disadvantages of this process are: a) halides are highly corrosive and are poisons for many types of catalysts b) it is difficult to separate the products and catalyst. These problems may be overcome by developing heterogeneous catalyst that can operate effectively without halide promoter. Studies at Boreskov Institute of Catalysis have shown that acidic cesium salts of 12-tangstophosphoric acid promoted with rhodium revealed high activity in the iodide-free carbonylation of the dimethyl ether (DME) to methyl acetate (MA) [1] that is one order of magnitude higher than the activity of the rhodium salts of the same acid supported on silica [2].

$$CH_3\text{-}O\text{-}CH_3 + CO \rightarrow CH_3\text{-}CO\text{-}O\text{-}CH_3$$

Investigations of the reaction over $1\%Rh/Cs_{1.5}H_{1.5}PW_{12}O_{40}$ catalyst were carried out at the excess CO, ratio DME : CO =1:19 and 1:10, temperature = 200, 220 and 250°C; space velocity = 2, 5, 10 liters $hour^{-1}$, pressure 10 atm. It was observed that DME conversion increased with temperature and contact time raise. It was also shown that DME conversion was inversely proportional to initial DME concentration and it did not depend on CO concentration. The rate constants and activation energy for DME carbonylation at the excess CO were evaluate assuming that the reaction is first order in DME. E=12,3 Kcal mol^{-1}. It may be suggested that DME carbonylation reaction occurs through Eley-Rideal route where CO molecule from gas phase interacts with adsorbed molecule of DME:

$$1.\ DME + [\ ] = [DME];\quad 2.\ [DME] + CO \rightarrow MA + [\ ].$$

References

[1]. G.G. Volkova, L.M. Plyasova, A.N. Salanov, G.N. Kustova, T.M. Yurieva, V.A. Likholobov, Catal. Lett. **2002**, *80*, 175; G.G. Volkova, L.M. Plyasova, L.N. Shkuratova, A.A. Budneva, E.A. Paukshtis, M.N. Timofeeva, V.A. Likholobov, Stud. Sur. Sci. Catal. **2004**, *147,* 403.

[2]. W.R. Wegman, European Patent 0353 722 **1989**.

Acknowledgements

This work is supported by Federal Target Program (FTP) ”Science, Academic and Teaching Staff of Innovative Russia for 2009-2013”. Contract P253.

GAS-PHASE HYDROFLUORINATION OF PERCHLOROETHYLENE INTO PENTAFLUOROETHANE: EXPERIMENT AND KINETIC MODELING

Reshetnikov S.I., Zirka A.A., Petrov R.V.

Boreskov Institute of Catalysis SB RAS, Pr. Akademika Lavrentieva 5, Novosibirsk, 630090, Russia, E-mail: reshet@catalysis.nsk.su

Under the Montreal Protocol On Substances That Deplete the Ozone Layer, the manufacture and consumption of ozone-depleting substances, such as chlorofluorocarbons, should be stopped within the next decade. This poses the challenging problem of gaining more detailed insight into the synthesis of nextgeneration, ethane-based Freons, such as pentafluoroethane (R-125). R-125 is obtained from perchloroethylene (PCE) in the presence of chromium-containing catalysts on various supports. In particular, chromium–magnesium catalysts are used for this purpose [1–3].

Here, we report the kinetics of PCE hydrofluorination into R-125 on a chromium–magnesium catalyst and discuss the reaction scheme taking into account formation of by-products.

Kinetic regularities of the vapor-phase hydrofluorination of perchloroethylene were studied at the total pressure of 0.4 MPa, temperature 330–390°C, contact time 0.3–16 s and the molar ratio HF : PCE = 6–50.

Based on the experimental data, the pathway of perchloroethylene fluorination with HF over a chromium-magnesium catalyst was identified. The process involves several consecutive reactions for the formation of main fluorination products and parallel reactions for the formation of by-products. It was shown that the total selectivity towards the main products decreases with the increase in temperature. It indicates that activation energies for the formation of by-products are higher than those for the formation of main products. Kinetic constants and the activation energy of the PCE conversion was obtained on the assumption of the first order of the reaction rate. The PCE consumption rate under these conditions is satisfactorily described by a first-order equation with respect to PCE.

References

[1]. US Patent 6165931, **2000**.
[2]. RF Patent 2179885, **2002**.
[3]. Zhul, Y., Fiedler, K., Rudiger, St., and Kemnitz, E., J. Catal., **2004**, 219, 8.

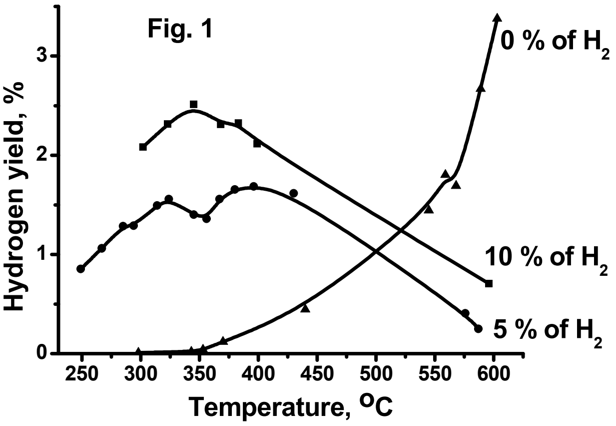
ON THE KINETICS AND REGULARITIES OF ETHYLENE GLYCOL OXIDATION INTO GLYOXAL

Salaev M.A., Kokova D.A., Novikov D.V., Krejker A.A., Menshchikova T.V., Knyazev A.S., Vodyankina O.V., Kurina L.N.

Tomsk state university, Tomsk, Russia, E-mail: mihan555@yandex.ru

The products of alcohol partial oxidation processes are valuable organic compounds (formaldehyde, acetone, etc). Glyoxal which can be produced by ethylene glycol oxidation [1] is a compound with good cross-linking properties providing its various applications. Because of high reactivity and low boiling point of glyoxal (50,4 °C, [2]) the common methods of experimental kinetic investigation do not allow obtaining correct data. Specifically, the most reliable flow circulating method is not suitable for kinetic studies of ethylene glycol oxidation because of high process exothermicity and possibility of polymerization and/or polycondensation between glyoxal and unreacted ethylene glycol, and other reactive products at elevated temperatures. One of the ways to overcome the problems mentioned is kinetic studies in non-isothermal conditions [3].

In the present work catalytic activity and kinetic regulations of catalytic systems of different granularity, representing Cu catalyst, bulk, freshly made and broken-in supported Ag catalysts prepared using sol-gel method mixed with quartz particles, were investigated in a flow fixed bed reactor in the temperature range between 250 and 600 °C at constant heating rate and $O_2/(CH_2OH)_2$ molar ratio between 0.8 and 1.6. Analysis of gas and liquid products was carried out using GC and HPLC methods. It was stated that small yields of products can be observed before light-off temperature was achieved. The main liquid products here were small equal amounts of glyoxal, glycolaldehyde and formaldehyde. This may be an evidence of ethylene glycol single center adsorption. When light-off temperature was achieved, significant increase in H_2 and carbon oxides yields, amounting to constant values at optimal temperatures, was observed. Glyoxal became the predominant liquid product. Small amounts of glycolaldehyde, formaldehyde, and organic acids were observed. Probably, a double center adsorption of ethylene glycol takes place in this temperature region. The maximal alcohol conversion and selectivity with respect to glyoxal were observed at elevated temperatures where external diffusion took place which was considered to be preferable in comparison with kinetic mode.



In the present work to itemize the process mechanism several gas and vapor additions, namely, H_2, CO, CO_2, water, were introduced into reaction mixture, replacing 5 to 10 % of nitrogen content. The by-product reactions, including CO oxidation and water-gas-shift reaction, were investigated over supported silver catalyst. When additional amount of H_2 was introduced into reaction mixture (Fig. 1), H_2 yield curve had maximum in the light-off region. During investigation of CO oxidation reaction, performed in the presence and absence of ethylene glycol vapor, it was shown that the share of the reaction is small, and catalyst surface is involved. Temperature-programmed reaction with MS was also used. It was stated that great amounts of CO may suppress the oxidation process and cause catalyst deactivation. It was stated that WGS reaction did not take place in the process. A mechanism of additives influence was also proposed.

On the basis of the results obtained and literature review the Langmuir-Hinshelwood mechanism of ethylene glycol oxidative dehydrogenation over silver-containing catalysts was proposed. A microkinetic model was developed, taking into account the data on catalyst surface structure. Adsorption equilibrium constants as well as thermodynamic parameters for key components of the model were calculated using statistical thermodynamic methods. Ground state energies for gas components were calculated using DFT approach. The rate expressions for slow and rate limiting stages were derived. Discrimination of kinetic models obtained was performed. Mathematical modeling of glyoxal synthesis reactor was carried out. The observed reaction kinetics parameters were determined on the basis of experimental results and compared to simulated data. Correlation between experimental and simulated results was achieved.

References

[1]. O.V. Magaev et al., Appl. Catal. A 344 (2008) 142–149.
[2]. Ulmann's Encyclopedia of industrial chemistry, Wiley-VCH, 2007.
[3]. F. Duprat, Chem. Eng. Sci., 57 (2002) 901-911.

Acknowledgements

This work was supported by Federal Agency for Science and Innovations (GC No. 02.523.12.3023), Federal Agency for Education (GC No. P998).

DIFFERENTIAL THERMAL ANALYSIS AND THERMAL GRAVIMETRY OF SOOT OXIDATION $MeAl_2O_4$ (Me=Mn, Fe, Co, Ni, Cd, Mg) SPINEL TYPE CATALYSTS

Zenon Sarbak

Laboratory of Adsorption and Catalysis in Environmental Protection, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland
sarbak@amu.edu.pl

As a one of the measure taken to protect the natural environment, the EU authorities have introduced limitations on the content of harmful substances, including diesel soot or particulates matter, in the vehicle exhaust emissions. This particulate matter composed mainly of the graphite o like soot. Some of this products contain polyaromatic hydrocarbons, heave metals, sulphates and water which are strongly adsorbed on the porous surface of soot. Because of high cancerogenic and mutagenic activity this soot must be removed from the exhaust gases. The much desired reduction of concentration of the soot is achieved by the engine construction improvement or by exhaust gases treatment by filtration and catalytic oxidation.

Our group has been working long time on soot removal using catalytic oxidation of carbonizate which can simulate in some extend Diesel soot.

This presentation reports results of the soot oxidation in the presence of spinel catalysts of $MeAl_2O_4$ type, where Me = Mn, Fe, Co, Ni, Cu, Zn, Cd and Mg.

The catalysts using aqueous solutions of nitrates of above metals. After drying at 110°C overnight the sample were calcinated at 1050°C for 4 h in oxygen atmosphere.

The differential thermal analysis (DTA) and thermal gravimetric (TG) measurements were carried our on the computerized Paulik-Paulik-Erdey OD-102 derivatograf (Hungary). The portion of well homogenized mixture of catalyst and carbonizate was placed in a ceramic crucible and heated to 1000°C at the rate 13° min^{-1} in air steam at the rate of 30 cm^3 min^{-1}. The DTA and TG curves were recorded.

Analogous measurmets in the same conditions were perforemed for the catalysts alone and the carbonizate alone. The carbonizate (Hajnowskie Zakłady Suchej Destylacji Drewna, Poland) was subjected to elemental analysis, which shows content of 78.64 mass. % C, 1.34 mass. % C and 1.7 mass. % N.

The DTA and TG methods have been to be fast and effective determination of catalysts activity in soot oxidation. All examined sample caused removal of soot, which depends on metal kind in alumina spinel. These differences are discussed in presentation.

A TiO_2/ADSORBENT PHOTOCATALYTIC SYSTEM: KINETICS MODELING AND EXPERIMENTS

Selischev D.S.[1], **Kozlov D.**[2]

[1]*Novosibirsk State University, Novosibirsk, 630090, Russia,*
e-mail: selishev@catalysis.ru
[2]*Boreskov Institute of Catalysis SB RAS, pr. Ak. Lavrentieva, 5,*
Novosibirsk, 630090, Russia

Photocatalysis on semiconductors is a good method of air and water purification from organic admixtures wich has been extensively developed over last decades [1]. Main efforts are focusing on the synthesis of highly active photocatalysts which are usually based on the anatase form TiO_2. At the same time adsorption properties of the photocatalytic system also influence on the rate of photocatalytic processes especially in the low concentration range which is obvious from the classic Langmuir–Hinshelwood (L.–H.) dependence of the product formation rate on the gas concentration of a substrate:

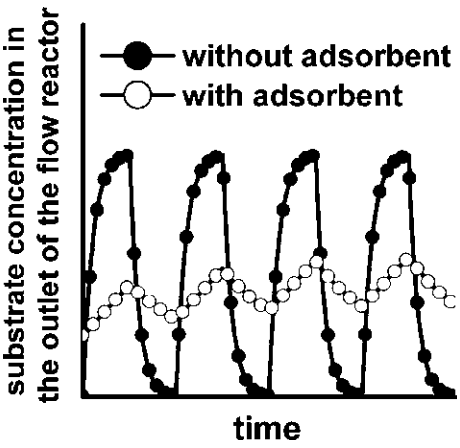
$$dP/dt = \frac{k \cdot K_{ads} \cdot A}{1 + K_{ads} \cdot A} \xrightarrow[K_{ads} \cdot A \ll 1]{} dP/dt \approx k \cdot K_{ads} \cdot A$$

In this case the rate of photooxidation is in direct proportion to the adsorption constant K_{ads}. Probably it is a reason of constantly growing interest to the combination of adsorption and photocatalysis in last years.

Combination of photocatalyst and adsorbent could give effect also in the case of highly concentrated pollutants. Adsorbent in this composite photocatalytic system could act as a center where organic molecules will be first adsorbed and then transferred onto the decomposition center, i.e. illuminated TiO_2, which is located on the adsorbent surface. In this case time of pollutants removal from gas or water phase could be considerable decreased.

In the first part of work influence of adsorbent on the kinetics of photocatalytic oxidation (PCO) processes was studied using the simple single and double stage reaction mechanisms with the adsorption stages corresponding to Langmuir model. Both static and continuous flow photocatalytic reactors were simulated.

It was found that in the static reactor in all cases the usage of adsorbent leads to the prolongation of substrate (A) removal and product (P) accumulation kinetic curves but the substrate concentration becomes lower during almost all photocatalytic process. Fitting of experimental data points of acetone photocatalytic oxidation reaction demonstrated a good correlation with proposed reaction mechanism. Calculated adsorption constants values are close to those reported in literature. The using of adsorbent in flow reactor leads to the decrease of maximum outlet substrate concentration in the case if the inlet substrate concentration is too high to be oxidized completely for one run.



Kinetics simulation in the case of photocatalytic reaction with intermediate demonstrates that adsorbent could accumulate additional intermediate quantity thus keeping catalyst surface more active and contributing to faster substrate (A) removal [2].

In the second part of work several composite TiO_2/adsorbent samples with various TiO_2 content were investigated. Purpose was to find the most active photocatalyst and to increase adsorption capacity of composite photocatalyst. TiO_2 deposition was carried out by thermal hydrolysis of $TiOSO_4$ in the presence of adsorbents: activated carbon (AC), SiO_2 and Al_2O_3. Synthesized photocatalysts were tested in the photocatalytic oxidation of acetone and cyclohexane vapors in static and flow reactors.

Kinetic curves of acetone and cyclohexane removal and CO_2 accumulation in a static reactor demonstrated complete pollutants mineralization. Synthesized photocatalysts demonstrated high adsorption capacity. Langmuir-Hinshelwood kinetic model was used to describe the dependence of photocatalytic oxidation rate on the substrate concentration. Obtained results show that adsorption constants for TiO_2/AC can be about 1.5 – 2 times higher than for pure TiO_2 in cyclohexane PCO.

References

[1]. O. Carp, C.L. Huisman, A. Reller, Prog. Solid State Chem. 32 (**2004**) 33–177.

[2]. D.S. Selishchev, P.A. Kolinko, D.V. Kozlov, *Applied Catalysis A: General* 377 (**2010**) 140-149.

Acknowledgements

The work is supported by Russian Federal Innovation Agency via the program ‘‘Scientific and Educational cadres’’. Authors also appreciate the grant program “U.M.N.I.K.” of “The Fund of Assistance to Development small Forms of the Enterprises in Scientific and Technical Sphere”.

PP-I-54

KINETICS OF AQUEOUS ALKALI OXIDATION OF NONYLPHENOL ETHOXYLATE ON PALLADIUM CATALYST

Staroverov D.V., **Varlamova E.V.**, **Suchkov Yu.P.**

D. Mendeleyev University of Chemical Technology of Russia, Miusskaya Sq. 9,
125047 Moscow, Russia; E-mail: stardv@pxty.ru

Aqueous alkali oxidation of ethoxylates on noble metal catalysts is the selective method of anionic modification of nonionic surfactants:

$RO(CH_2CH_2O)_{n-1}CH_2CH_2OH + O_2 + NaOH \rightarrow RO(CH_2CH_2O)_{n-1}CH_2COONa + 2\ H_2O.$

Reaction products are the ether carboxylates labelled as a perspective class of surfactants with expanding application range. Valuable properties of ether carboxylates are determined by a structure of molecules: polyether chain is the screen softening the antagonism between a hydrophobic radical and anionic (carboxylate) function. Sometimes ether carboxylates are called cryptoanionic surfactants to underline their soft anionic nature. Usage of a method of direct ethoxylates oxidation by oxygen allow to refuse additional reagents for synthesis of ether carboxylates and to avoid formation of accompanying impurities and a waste. The kinetics of ethoxylates oxidation on palladium catalyst has been investigated on example of Neonol AF9-6 (nonyl phenol ethoxylate with ethoxylation degree 6). The catalyst is 2 % Pd on activated carbon.

Ethoxylates and ether carboxylates solutions possess the high foaming ability imposing unmanageable restrictions on hydrodynamics as well as on mass and heat transfer. Therefore in the network of present study we have developed the experimental technique for carrying out of reaction on rotatory film device with the volumetric control. Using this technique we have excluded foaming and provided a kinetic mode of process.

Other feature of ethoxylates and ether carboxylates aqueous solutions is existence of the isotropy top temperature limit ("cloud point"). Cloud point increases with growth of conversion of ethoxylate into ether carboxylate. In the course of oxidation it leads to change of reaction solution phase state: the unstable dispersion of coacervate (hydrated "organic" phase of a surfactant) turns to an isotropic micellar solution. Accordingly, we have differentiated "emulsion" and "micellar" phase modes of reaction. It is established that oxidation reaction is accompanied by the reversible catalyst over-oxidation leading to decrease of activity in both phase modes.

It is established that both target oxidation reaction, and the processes affecting catalyst over-oxidation degree, proceed only on the catalyst surface wetted with an "aqueous" phase or a micellar solution. An "organic" phase at "emulsion" mode adhesionally screens a catalyst surface both in relation to target reaction, and in relation to reversible over-oxidation. Process is complicated by expanding ("swelling") of "organic" phase with growth of ethoxylate conversion up to phase transition. The simulation of a "organic" phase volume fraction and a "aqueous" wetting fraction of the catalyst surface is offered.

The basic reaction has the first orders to oxygen and ethoxylate adsorbed on "aqueous" wetted catalyst surface in both phase modes. The conclusion is drawn that a limiting stage of reaction is oxidation of ethoxylate adsorbed on a non-over-oxidated catalyst surface by physically sorbed molecular oxygen. The method for simulation of ethoxylate and ether carboxylate active concentrations in "aqueous" phase and the micellar solution based on the Holland and Rubingh thermodynamic approach is offered. For simulation of ethoxylate oxidation rate on the "aqueous" wetted catalyst surface we have used a Langmuir-Hinshelwood model.

Over-oxidation rate of the catalyst exponentially grows with oxygen concentration increasing, and rate of activity restoring is proportional to concentration of alkali and ethoxylate surface concentration. The conclusion is drawn that catalyst over-oxidation is caused by transfer of dissociatively sorbed oxygen from surface to the subsurface layer of metal. The over-oxidated catalyst can slowly be restored owing to reverse transfer of the subsurface oxygen onto external surface of metal. However restoring proceeds much faster at the expense of reaction of the adsorbed ethoxylate and the subsurface oxygen with the assistance of alkali. Simulation of balance of oxygen reversible transfer to the subsurface layer of the metal based on a Frumkin formalism.

PP-I-55

KINETIC CHARACTERISTICS OF THERMAL DECOMPOSITION OF DITHIOL COMPLEXES OF Fe(II)

Sugurbekova G.[1], **Mazhibaev A.**[1], **Shomanova Zh.**[1], **Sugurbekov Y.**[2]

[1]*Taraz State University named after M. Kh. Dulaty, Kazakhstan*
gulnar-sugur@yandex.ru
[2]*Razakh-British Technical University, Kazakhstan*

The results of thermal decomposition of 2,3-dimerkaptopropansulfonate (unithiol-L) complex of iron are represented.

The thermal analysis of the complex have been carried out by DTA and DTG methods on the derivatograph Q-1000 (Paulik-Paulik-Erdei) via nonisothermic heating till the full destruction in the oxidizing atmosphere under atmospheric pressure and humidity. Al_2O_3 calcinated at 1000°C has been used as a comparative standard. The chain resistance of DTA was 1/10 and DTG as well, the heating velocity was 10° C per min.

The identification of intermediate and final products of thermal decomposition $[FeL_2H_2O]$ H_2O have been carried out by chemical, X-ray phase and IR-spectroscopic methods.

Endotermic effects at nearby 100°C and 240°C on the DTA thermal destruction curve have been related to the dehydration on process of $Na_2[FeL_2H_2O]$ H_2O (fig.1).

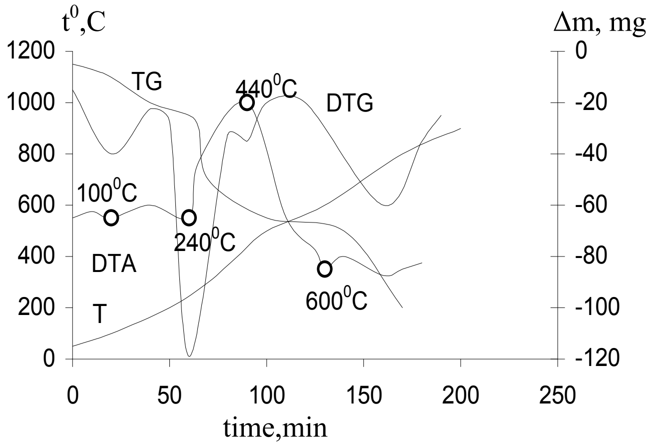


Fig. 1 – Derivatogramme unithiol complex of iron

Exotermic effects at 400°C and 440°C, blocking each other, are forming big maximum having a break in the area of 400°C and correspond to the thermal destruction of coordinated molecules of ligand followed by sulphide and sulphate of iron. It must be marked that exoeffect at 400°C is faint. May be the process corresponding to these effects, are energetically close. The deep endoeffet on the DTA curve at 600°C corresponds to the destruction of the iron sulfate $FeSO_4$ formed to Fe_2O_3.

The valent - fluctuations v_{as} in the IR spectrum at the frequency range of 1050 - 1170 sm^{-1} of the thermolysis products correspond to the fluctuations of SO_4^{2-} group that twestify the oxidation of sulfone group of thiol to SO_4^{2-} and formation of sodium sulphate absorption bond at 1000 sm^{-1} in the IR spectrum of destruction products. The absorption bonds at 600-635 sm^{-1} correspond to the sulfide formation. Thus, the chemical mechanism thermal destruction of unithiol complex of iron studied by DTA, IR-spectroscopic and X-ray phase analysis is represented by the following scheme:

$$Na_2[FeL_2H_2O]H_2O \xrightarrow{78\text{–}160°C} Na_2[FeL_2H_2O]+H_2O \xrightarrow{160\text{–}285°C} Na_2[FeL_2]+H_2O \xrightarrow{400°C}$$

$$Na_2SO_4+FeS+6CO_2\uparrow+H_2O+4H_2S\uparrow \xrightarrow{440°C} FeSO_4 \xrightarrow{600°C} Fe_2O_3+(SO_2,\ SO_3,\ O_2)\uparrow$$

The kinetic parameters of activation process of dehydration of iron complex are $Na_2\,[FeL_2H_2O]\,H_2O$ are represented in table 1.

Table 1 - The kinetic characteristics of the thermal decomposition of the iron complex

Complex	T_m, °C	E_a, kJ/mol	$\lg A_0$, c^{-1}	$\ln k$, c^{-1}	$-\Delta S^{\neq}$, J/mol·K	$\Delta H^{\neq}$, kJ/mol
$Na_2[FeL_2H_2O]H_2O$	100	35,1	12,0	1,7	155,1	32,0
	240	8,4	4,1	2,6	233,3	4,1
	440	16,38	5,41	2,59	231,42	10,58
	600	63,71	12,5	3,72	172,26	56,45

The dehydration reaction of these complexes is developed by steps. Values The activation energy (E_a) values are essentially decreased for waterless complex, namely from 35,1 to 8,4 kJ/mol. The separation of molecule under water heating conditions the weakness of some bonds in the complex that leads the further process with smaller energy of activation. Value of a speed constant of dehydrotation reaction of speed lnk is increased from 1,7 to 2,6 c^{-1}.

By consideration enthalpy ($\Delta H^{\neq}$) and entropy ($\Delta S^{\neq}$) of activation values one can conclude, that enthalpy and entropy factors for waterless complexes compensate each other and probably compensatory effect in the kineticl process can be observed.

PP-I-56

A STUDY OF LIGHT ALKANE TRANSFORMATIONS IN REACTIVE NON-THERMAL PLASMAS

Suslov A.[1], Kudryashov S.[2], Ryabov A.[2] and Kutenkov V.[1]

[1] *Institute of High Current Electronics, Tomsk, Russia, suslov@to.hcei.tsc.ru*
[2] *Institute of Petroleum Chemistry, Tomsk, Russia*

The processes of C_3-C_4 hydrocarbons (HC) conversion to liquid products has been considered in the glow-type barrier discharge (BD) plasmas at the ambient gas temperature under atmospheric gas pressure. To this end a multi-cell BD-based reactor system of plane design has been developed with a discharge gap in each section of 1 mm in length. A schematic diagram of the experimental assembly (a) with an example of glow-type gas discharge inside single DBD cell (b) are shown in the figure 1.

The C_3-C_4 mix and gaseous mixtures of C_3-C_4 with O_2 were studied for production of oxygenated and long-chain hydrocarbons. A repetitive pulsed power supply provided uniform deposition of 1 J of electric energy into reactor with a repetition rate of 1 kHz. The output product concentrations were detected using gas-liquid chromatography techniques. To analyze the reaction mechanisms of C_3-C_4 transformations a numerical model of plasma chemical reactor has been developed. It comprised kinetic calculations of conversion processes, a self-consistent simulation of BD and pulsed power supply in conjunction with reactor system. The modeling allowed definition of basic reaction mechanisms and concentrations of the output species.

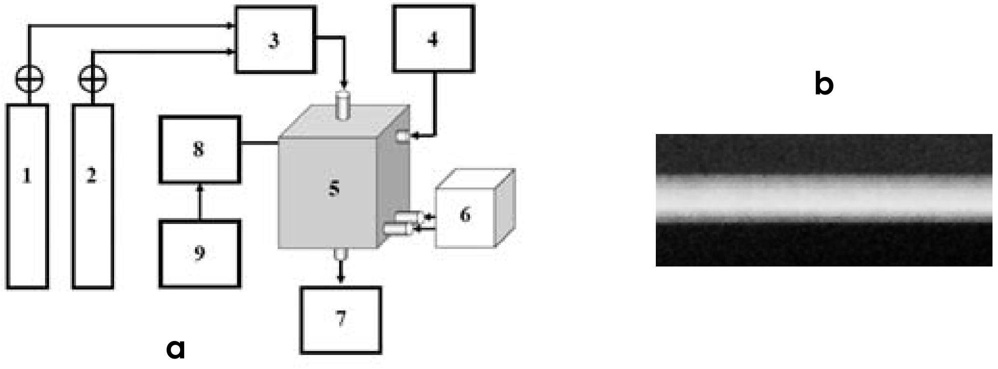


Fig. 1. Schematic representation of experimental device with BD reactor of planar design (a). 1-2 – hydrocarbon and oxygen gas cylinders with standard pressure regulators; 3 – mixing cell; 4 – high voltage generator; 5 – reactor with a heat exchanger; 6 – thermostat; 7 – receiver; 8 – a liquid pump; 9 – sorbent container (liquid HC); appearance of the glow-type BD in a single cell (b).

The experiments and simulation have shown, that main products of oxidative conversion are hydroxyl and carbonyl compounds ($RH:O_2=1:2$, table 1) and long-chain HC of isomer structure for propane-butane mix. Respective end product concentrations obtained in experiments are shown in the table 1.

A leading role for oxygenated HC formation is played by the reaction of disproportionation of peroxide radicals:

$$2ROO^{\cdot} \rightarrow ROH + RC(-H)O + O_2.$$

In our conditions it represents chain termination process which results in formation of alcohols, aldehydes and ketones. Isomer HC formation occurred in oxygen deprived C_3-C_4 mix predominantly via recombination of alkyl radicals.

Table 1. Composition of oxygenated HC (experiment).

Products	Concentrations, % mass
aldehydes	31,1
ketones	17,1
alcohols	51,8

The results obtained indicate that light hydrocarbons C_3-C_4 could be efficiently transformed to liquid oxygenated products via short-chain reaction mechanism. Compositions of the end products derived from numerical calculations have a good agreement with experimental data.

PP-I-57

KINETIC REGULARITIES OF N-BUTANE ISOMERIZATION OVER MORDENITE-ZIRCONIA CATALYST

Tagiyev D.B., **Starikov R.V.**

Institute of Petrochemical Processes of Azerbaijan NAS, dtagiyev@hotmail.com

Introduction

It has been shown in publications [1, 2] that promotion of dealuminated mordenite by zirconia and sulfate-ions results in a considerable increasing of zeolite isomerizing activity and allows to perform isomerization of *n*-butane at lower temperatures. The results of investigation of kinetic regularities of the process essential for understanding of action mechanism of sulfated mordenite-zirconia catalysts in *n*-butane isomerization are presented in the given paper.

Experimental

The kinetics study of reaction was carried out in a flow microreactor at 0.1MPa pressure and temperature range 473-513 K. Before testing a catalyst was heated in a dry air stream at 773 K for 3 hours. Partial pressures of *n*-butane and hydrogen were varied in the range 0.01-0.08 and 0.01-0.04 MPa, respectively. For ensuring of velocity constancy of gas stream nitrogen was used as an inert diluent. The products of reaction were analyzed by gas chromatography method.

Results and discussion

The dependences of main products formation velocities of *n*-butane conversion (isobutane, isopentane, propane) on partial pressures of reactants were determined at moderate conversion of *n*-butane, i.e. in the range of pseudo zeroth order of reaction. The obtained results are presented in Table 1 at temperature of 473 K.

Table 1. Influence of reactants partial pressures on *n*-butane conversion and reaction rate (temperature - 473 K, stream rate - 500 ml·h^{-1})

Partial pressures, MPa		Conversion of *n*-butane, %	Reaction rate, $W_i \cdot 10^4$ mole·g^{-1}·h^{-1}		
$P_{n-C_4H_{10}}$	P_{H_2}		isobutane	isopentane	propane
0.01	0.01	2.6	0.28	0.04	0.03
0.02	0.01	2.9	0.67	0.09	0.06
0.04	0.01	3.2	1.41	0.23	0.17
0.06	0.01	3.7	2.46	0.35	0.27
0.08	0.01	5.1	4.58	0.470	0.47
0.01	0.02	1.9	0.21	0.03	0.02
0.01	0.04	1.4	0.15	0.02	0.01

In the studied range of temperatures formation rates of all products are increased with growth of n-butane partial pressure. Influence of hydrogen partial pressure on reactions rates depends on temperature: at 473 K negative order on hydrogen is observed which with increasing of temperature is approached to zeroth one. Therefore, dependences of formation rates of *n*-butane conversion products on partial pressures of reactants are described by one total equation:

$$W_i = k_i P^n_{n-C_4H_{10}} P^m_{H_2} \qquad (1)$$

Reaction orders n and m were determined from the slops of lines fitting rate vs. reactant partial pressures on logarithmic coordinates. It has been found, that for all reaction products and at different temperatures n has 1.3±0.2 value, at 473 K m is equal to -0.5±0.1 and with increasing of temperature is approached to zero. Apparent activation energies calculated from Arrhenius plots of reaction rates for isobutane, isopentane and propane formation are equal to 72 ± 4; 102 ± 6 and 116 ± 6 kJ mole^{-1}, respectively.

Different kinetic models of the process were considered. It has been shown that the reaction has complex nature and it specific mechanism depends on both catalyst nature and process operation conditions. Both monomolecular and bimolecular mechanism of reaction may be predominant with changing of temperature. As the reaction network is complex and the primary and secondary reactions not resolved, the kinetic results cannot be regarded as more than just empirical; they represent overall reactions and not a resolution of the individual reactions. Nevertheless, on the basis of obtained results a search of the promoters, permitting to decrease an isomerization reaction temperature and to provide a higher selectivity, may be considered as the perspective approach to a development of the effective mordenite catalysts for *n*-butane isomerization.

References

[1]. D.B. Tagiyev, R.V. Starikov, A.A. Imanova. Stud. Surf. Sci. Catal., **2005**,158, 1685.

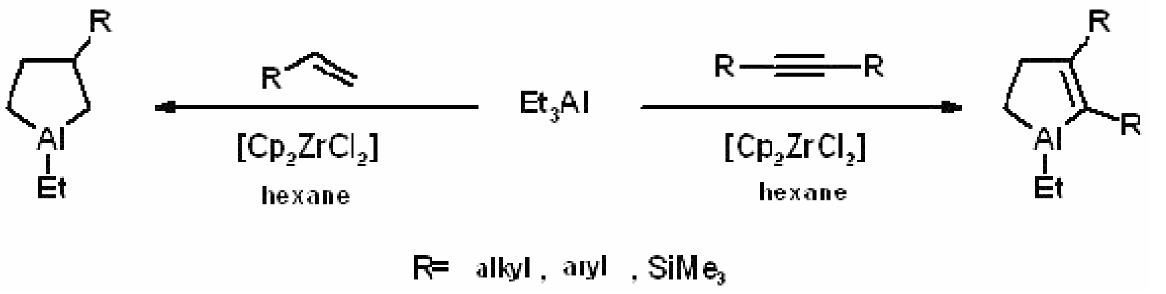
[2]. D.B. Tagiyev, R.V. Starikov, A.A. Imanova, M.I. Rustamov. Petroleum Chemistry, **2008,** 48, 29.

THE KINETIC MODEL OF CYCLOALUMINATION REACTION WITH OLEFINS AND ACETYLENES

Tikhonova M.V., Kadikova R.N., Ramazanov I.R., Gubaydullin I.M.,
Lavrenteva J.S., Spivak S.I., Dzhemilev U.M.

Institute of Petrochemistry and Catalysis, Russian Academy of Sciences,
141, prospect Oktyabrya, Ufa, 450075, Russian Federation, tiny_daisy@mail.ru

The purpose of work is the identification of the mechanism kinetic parameters of the cycloalumination (CA) reaction of olefins and acetylenes olefins in the presence of a catalyst $Cp_2Zr_2Cl_2$.



It was shown in the paper that using of mathematical modeling methods with parallel programming technologies is effective for studies of reaction mechanisms of metal complex catalysis [1].

The study had several stages: conducting chemical experiments, developing a mathematical description of the CA reaction, designing and implementation of relational database system of kinetic studies of the CA reaction and conducting a sequential and parallel calculation using graphics processing unit (GPU).

A comparative analysis of experimental and calculated data was done on the reactivity of olefinic and acetylenic compounds in the CA reaction.

Temperature varied in the range from 0 to 50°, the initial catalyst concentration ranged from 0.02 to 0.06M, Et_3Al ranged from 0.2 to 1,0M. The relative error between the experimental and calculated concentration values of the CA reaction products is no more than 7%.

The found activation energy values and obtained dependence of stage rates on the reaction time showed that relative reactivity decreases for olefins in the series: Octene-1 > α-allylnaphthalene > Styrene > Allylbenzol > Norbornene > >Trimetivinylsilane, and acetylenes in the series: Octyne-1 > Phenylacetylen > >Octyne-4 > Butyl(trimethyl)acetylene > Octyl(trimetilsilin)acetylene.

Headings

Advances in Chemical Reactors Fundamentals

- Chemical Reactors Kinetics

References:

[1]. The Mechanism of Cp_2ZrCl_2-Catalyzed Alkene Cycloalumination with Triethylaluminum to Give Alumacyclopentanes. Balaev A.V., Parfenova L.V., Gubaidullin I.M., Rusakov S.V., Spivak S.I., Khalilov L.M., Dzhemilev U. M. *J. Doklady Physical Chemistry,* **2004**, p. 279-282.

[2]. The theory and practice of parallel computing. Binomial. Knowledge Lab. Gergel V.P., **2007**

PP-I-59

KINETIC MECHANISMS OF CONVERSION OF NATURAL GAS INTO AROMATIC COMPOUNDS OVER MODIFIED PENTACYL

Vosmerikova L.N.[1], **Vosmerikov A.V.**[1], **Litvak E.I.**[2]

[1]Institute of Petroleum Chemistry, Siberian Branch of the Russian Academy
of Sciences, 634021, 4, Akademichesky Avenue, Tomsk, Russia
[2]Tomsk Polytechnic University, 634050, 30, Lenin Avenue, Tomsk, Russia
E-mail: lkplu@ipc.tsc.ru

The development of new gas and gas condensate fields and their bringing into service raise the problem of rational use of low-molecular weight methane-associated paraffins C_2-C_4. Taking into account the scale of natural gas production, the leight alkanes are an important potential source of raw material for chemical industry. Of particular interest is an one-stage catalytic synthesis of aromatic hydrocarbons from gaseous paraffins and olefins.

The investigations have revealed the possibility to obtain the aromatic compounds C_6-C_9 and above from light satured hydrocarbons in presence of modified high-silica zeolithes. So, the development of the process of components of natural gas over zeolithe catalysts is an actual task, which creates the prerequisites both for resource-saving under growing oil deficit conditions and for effective use of relatively cheap gaseous hydrocarbons as a raw material for valuable chemical substances of different purposes. The aromatization of the of natural gas components is characterized by complex kinetic mechanisms because during this processus the hydrocarbons of different homologue series participate in several types of chemical reactions on the active catalytic centres simultaneously. Therefore, it is advantageous to study the kinetics of this process via the methods for mathematical simulation using experimentally revealed dependancies.

To study the kinetics of conversion of low alkanes into aromatic hydrocarbons the experiments were carried out in a laboratory flow type quartz reactor at the reaction temperature of 600-750 °C, the feedstock space velocity 500-5000 h^{-1} and atmospheric pressure. The high-silica ZSM-5 zeolite (molar ratio SiO_2/Al_2O_3=40), which contained 0.5 wt % gallium oxide and 4.0 wt % molybdenum oxide was used as a catalyst. The volume of catalyst in the reactor was varied from 0.5 to 4.0 cm^3.

Taking into account the stability of catalyst operation, the duration of experiment was established in dependence on the process conditions. To evaluate the catalytic activity of the samples in the natural gas conversion process, the degree of conversion of a component of the feed gas was determined and the yield of gaseous and liquid products, as well as the selectivity for aromatic hydrocarbons was calculated. During the aromatization of low alkanes the gaseous and liquid products were formed. Gas-chromatographic analysis has been demonstrated the presence of hydrogen, methane, alkanes and alkenes C_2-C_4 in gases. The liquid products are presented by benzene and alkylbenzenes C_7-C_9, naphthalene and metylnaphtalenes.

The table gives the results of kinetic study, obtained during the aromatization of natural gas components at the temperature of 700 °C.

Table Content of the products of natural gas conversion over 0.5% Ga-4.0% Mo/ZSM-5 catalyst at different contact time

Products yield (wt %)	Contact time (s)			
	0.7	0.9	1.8	3.6
Hydrogen	2.09	2.18	2.48	2.86
Alkanes	84.03	83.64	82.25	80.26
Alkenes	4.76	4.39	3.30	2.33
Benzene	7.74	7.99	9.92	11.86
Toluene	0.48	0.51	0.43	0.33
Naphthalene	0.87	1.25	1.56	2.31
Methyl- и dimethylnaphthalenes	0.03	0.04	0.06	0.05
Conversion of natural gas, %	16.0	16.4	17.8	19.7
Selectivity for aromatic hydrocarbons, %	57.0	59.7	67.2	73.9

The increase in the degree of conversion of initial feedstock components with the increasing contact time is observed. The yield of benzene and naphthalene in liquid reaction products increases, the content of toluene reaches a maximum. By secondary conversions the rate of toluene consumption surpasses the rate of its formation with the increasing contact time. The primacy of olefin hydrocarbons formation is testified by the decrease in yield of these intermediate products with the increasing contact time. The further transformations of olefin hydrocarbons result in the formation of aromatic hydrocarbons. With the increasing contact time the concentration of hydrogen, presented in reaction products also increases, which indicates that the reactions of dehydration of initial alkanes and dehydrocyclization of the formed olefins over modified pentacyl are intensive.

Thus, the experimental findings of investigation of conversion of natural gas into 0.5% Ga-4.0%Mo/ZSM-5 aromatic hydrocarbons allow developing a kinetic model of the process, to evaluate the influence of kinetic parameters, and to create a mathematic model of reactor block.

Acknowledgements

The work was supported by grant of the Program Presidium of RAS (grant № 27.50).

PP-I-60

TWO CFD-BASED STEPS TO SOLUTION OF PROBLEM OF OPTIMAL TWO-STAGE CATALYTIC AMMONIA OXIDATION SYSTEM DESIGN

Zakharov V.P., **Isupova L.A.**

Boreskov Institute of Catalysis SB RAS, 5, Akad. Lavrentiev Ave.,
Novosibirsk, 630090, Russia, xap@catalysis.ru

Two-stage catalytic system, consisting of a platinum gauze pad and an oxide honeycomb bed, allows to decrease platinum loads and losses and is widely used in ammonia oxidation process in a weak nitric acid large-scale production. Unfortunately, the system is applied without proper theoretical foundation of its composition, although attempts of consideration of some aspects of such foundation were made [1-5]. Therefore the development of complete CFD-based model of two-stage catalytic system for ammonia oxidation process is still actual.

Two steps in development of such model were made in the paper that allows to get the valid answer to the question: «How many platinum gauzes can be replaced with honeycomb catalyst depending on its geometry and selectivity?». Each step was devoted to consideration of individual aspect of simulation of mass transfer process in the each stage.

The first step allows to clarify whether knowledge of the ammonia conversion degree over a single weaven gauze is sufficient to calculate correctly the ammonia conversion degree over whole gauze pad. To reveal the influence of interstitial flow conditions on the mass transfer, the total ammonia conversion degrees over neighbour gauzes of a different gauze pads thickness were analyzed. The pads consist of model geometry gauzes, because of otherwise it is impossible to provide their spatial periodicity, that is an essential difficulty in the calculations conducting. Model gauze consists of two contacting rows of equidistant wires. Rows wire directions are orthogonal. To understand the difference between single weaven gauzes of the real or model geometries the mass transfer characters were obtained and compared with each other. They were also compared with characters calculated according to the simplest gauze model based on gauze notion by assembled parallel cylinders [6]. Mathematical model was based on assumptions that mass transfer limitation approach is just, gauzes surface is smooth and gas flow is isothermal. Two last assumptions are not too strong, so far as the last gauzes (that are substituted with honeycomb catalyst) acting by residual, quite small, ammonia amount only and, as a consequence, oxidation reaction heat production and catalytic corrosion are highly small.

The second step allows us to reveal the side homogeneous reaction of nitrous oxide with ammonia in honeycomb channels contribution to the nitrous oxide yield. This step based on the ideal honeycomb catalyst model. Such catalyst is characterized with top activity and selectivity. It means that, firstly, its activity is enough for providing of a zero ammonia concentration at a honeycomb catalyst surface (i.e. mass transfer limitation approach is just), and, secondly, that ammonia completely converts to nitrous oxide. Limitation of oxygen transport rate to channel wall was not taken into account in the model. Obtained data for different shape channels are compared with each other in the paper. Comparison was made at identical reaction mixture mass flow rate over honeycomb cell and channels density per square inch. Inlet ammonia and nitrous oxide concentrations in the channel (i.e. in the gas mixture that leaves platinum gauzes) were varied. Gas flow was supposed as isothermal due to low inlet ammonia concentration (by the same reason that was considered in the first investigation step).

Models parameters used in calculations were corresponded to commercial plants UKL-7 (P=7 atm, T=900°C) and AK-72 (P=3,5 atm, T=850°C) conditions at corresponding values of superficial gas velocities.

Calculations were carried out at ANSYS FLUENT 6.3.26 program at cluster system NCS-160 and server SMP4x64 of Siberian Super-Computer Center of SB RAS.

References

[1]. Zakharov V.P., Zolotarskii I.A., Kuzmin V.A. CFD simulation of “gauze pad – honeycomb” catalytic system//Chem. Engng J. 91 (2003) 249-255.

[2]. Golovnya E.V., Brustein E.A. Two-stage ammonia oxidation system with non-platinum second stage honeycomb catalyst optimization//Catalysis in industry 3 (2004) 9-14 (in Russian).

[3]. Vanchurin V.I., Golovnya E.V., Brustein E.A. Ammonia oxidation over **oxide** honeycomb catalyst//Catalysis in industry 5 (2006) 52-57 (in Russian).

[4]. Beskov V.S., Brustein E.A., Golovnya E.V., Vanchurin V.I. Simulation of process of ammonia oxidation over platinoid gauzes//Catalysis in industry 2 (2008) 31-36 (in Russian).

[5]. Isupova L.A., Sutormina E.F., Zakharov V.P., Rudina N.A., Kulikovskaya N.A., Plyasova L.M. Cordierite-like mixed oxide monolith for ammonia oxidation process//Catalysis Today 1475 (2009) 5319-5323.

[6]. Heat-exchangers handbook, vol.1, M: Energoatomizdat, 1987, pp. 247-248 (in Russian).

PP-I-61

A NEW METHOD FOR SIMULATING OF REFORMING PROCESS IN INDUSTRIAL REACTORS

Zhapbasbayev U.K.[1], **Rakhmetova K.B.**[2]

[1]Kazakh-British Technical University, Tolebi str. 59, Almaty, 050000, Kazakhstan,
E-mail: U.Zhapasbayev@kbtu.kz
[2]Kazakh National University, Almaty, Kazakhstan

Catalytic reforming is one of important processes of oil refining industry [1, 2]. The process is carried out in a system of nonheated consistently connected reactors with fixed bed of catalyst. There is product warming between reactors.

In the known works [1] reforming reactors are calculated by zero-dimensional scheme. The zero-dimensional methods calculate balance of material and heat flows at input and output of the reactor, they does not allow to define distributions of flow velocity, concentration and temperature of reaction mixture in catalyst bed.

The mathematical model describing physical process consists of motion equations and heat-mass transfer, both in free parts of the reactor, and in a catalyst layer. The system of motion equations is considered with the biphase model of heat and mass transfer in the catalyst layer, received by the averaging method on phases of local volume of porous medium.

$$\rho\frac{dV_i}{dt}=-\frac{\partial p}{\partial x_i}+\frac{\partial}{\partial x_j}\left[-\frac{2}{3}\mu\,\frac{\partial V_k}{\partial x_k}\delta_{ij}+\mu\left(\frac{\partial V_i}{\partial x_j}+\frac{\partial V_j}{\partial x_i}\right)\right]-\left(\zeta_1+\zeta_2\,|\vec{V}\,|\right)\rho V_i$$

$$\frac{\partial\varepsilon\rho}{\partial t}+\frac{\partial\varepsilon\rho V_i}{\partial x_i}=0$$

$$\rho u\frac{\partial c_N}{\partial z}+\rho v\frac{\partial c_N}{\partial r}=\frac{\partial}{\partial z}\left(\rho D_z\frac{\partial c_N}{\partial z}\right)+\frac{1}{r}\frac{\partial}{\partial r}\left(\rho D_r r\frac{\partial c_N}{\partial r}\right)+W_N$$

$$\rho u\frac{\partial c_A}{\partial z}+\rho v\frac{\partial c_A}{\partial r}=\frac{\partial}{\partial z}\left(\rho D_z\frac{\partial c_A}{\partial z}\right)+\frac{1}{r}\frac{\partial}{\partial r}\left(\rho D_r r\frac{\partial c_A}{\partial r}\right)+W_A$$

$$\rho u\frac{\partial c_{Par}}{\partial z}+\rho v\frac{\partial c_{Par}}{\partial r}=\frac{\partial}{\partial z}\left(\rho D_z\frac{\partial c_{Par}}{\partial z}\right)+\frac{1}{r}\frac{\partial}{\partial r}\left(\rho D_r r\frac{\partial c_{Par}}{\partial r}\right)+W_{Par}$$

$$\rho u c_p\frac{\partial T}{\partial z}+\rho v c_p\frac{\partial T}{\partial r}=\frac{\partial}{\partial z}\left(\lambda_z\frac{\partial T}{\partial z}\right)+\frac{1}{r}\frac{\partial}{\partial r}\left(\lambda_r r\frac{\partial T}{\partial r}\right)+I_{N\to A}(\omega_1-\omega_5)+I_{Par\to N}(\omega_2-\omega_4)+I_{N\to G}\omega_3+I_{Par\to G}\omega_6$$

where $\zeta_1=150(1-\varepsilon)^2\upsilon/(d_p^2\varepsilon^2)$, $\zeta_2=1{,}75(1-\varepsilon)/(d_p\varepsilon)$ - expressions of Ergun equations, V_i - velocity components, m/s, p - pressure, Pa, μ - dynamic viscosity coefficient, kg/(m·s), ρ - density of raw, kg/m^3, c_N, c_A, c_{Par} - concentrations of naphthenes, aromatics, paraffins accordingly, kmol/kg, c_p - thermal capacity of gas, kJ/(kg·K), *T* - temperature, K, D_{eff} - effective diffusion coefficient, m^2/s, λ_{eff} - effective thermal conductivity, Wt/ (m*K), *I* - heat of reaction, kJ/kmol.

At $\varepsilon = 1$ the equations system transfers to usual Navie-Stoks equations and it applicable to flow in free parts of reactor, and at $\varepsilon < 1$ it describes the flow in catalyst layer.

Change rates of concentration of naphthenes, aromatic, paraffins will be written as [3].

Diffusion and heat conductivity coefficients are equal to diffusion and heat conductivity coefficients of mixture in granular layer they are found according to experimental data [4]:

$$D_{z,r} = A_0 D_0 + B_0 \left|\vec{V}\right| d \quad \lambda_{z,r} = \lambda_0 + C_0 \left|\vec{V}\right| \rho c_p d \ ,$$

where D_0, λ_0- diffusion and heat conductivity coefficients, *d* – diameter of catalyst grain, A_0, B_0, C_0 - empirical constants.

The developed theory can be used for the analysis of working processes in reforming reactors and allows receiving the following results:

1. The developed mathematical model consists of motion, heat and -mass transfer equations both in free parts of the reactor, and in a catalyst layer. The reacting mixture flow is defined by solution of Navie-Stocks equations in free parts and by solution of Ergun filtration equation in granular layer. Heat-mass transfer processes are described by monophase model with effective diffusion and heat conductivity coefficients in granular layer of reactor. This generalized mathematical model allows to construct the effective method for solving of equations system which satisfies to conjugate conditions on mediums interface.

2. The calculation data describes flow aerodynamics in free parts of reactor, reacting mixture distribution in catalyst layer, reaction rates of naphtha mixture conversion in catalyst layer, namely, conversion of naphthenes and paraffins to aromatics. The results show that macroscopically non-uniformities of velocity distributions of reacting mixture in catalyst layer exist. In one's part they cause non-uniformities of concentrations and temperature distributions and decrease conversion degree of oil products.

References

[1]. Kuznetsov A.A., Kagermanov S.M., Sudakov Ye.N. Calculations of oil refining industry processes and devices. Leningrad: Khymya, **1974** /in Russian/.

[2]. Rabynovitsh G.G., Ryabykh P.M., Khokhryakov P.L. Calculations of main oil-refining processes and devices. Moscow: Khymya, **1979** /in Russian/.

[3]. Smith R.B. Kinetic analysis of Naphtha reforming with platinum catalyst // Chem. Eng. Prog. **1959.** Vol. 55, PP. 76-80.

[4]. Aerov M.E., Todes O.M., Narynsky D.A. Fixed bed devices. Leningrad: Khymya, **1979** /in Russian/.

PP-I-62

STUDY ON EXOENZYMATIC KINETICS OF AUTOTHERMAL THERMOPHILIC AEROBIC DIGESTION FOR PRE-TREATING KLEBSIELLA PNEUMONIAE

Jing-Ming Liu[a,b], **Dong-Dong Sun**[a], **Hui Liu**[a], **Ying-Bing Nie**[c], **Zhirong Zhu**[b,*]

[a] *School of Chemical Engineering, Northeast Dianli University, Jilin 132012, China.*
[b] *Department of Chemistry, Tongji University, Shanghai 200092, China.*
[c] *Jilin Vocational College of Industry and Technology, Jilin132013,China.*
**Corresponding author: zhuzhirong@tongji.edu.cn*

Introduction

1, 3-propanediol (1, 3-PD) is an important chemical, and the bio-fermentation for producing 1, 3-PD by Klebsiella Pneumoniae is also exclusively the most efficient process [1]. Klebsiella Pneumoniae strains belong to genus Klebsiella, which is a kind of gram stain-negative and opportunistic pathogen and can cause a large number of serious diseases. The traditional way to treat infectious pollutants is to incinerate them, wasting a lot of energy and polluting environment. Autothermal Thermophilic Aerobic Digestion (ATAD) has a self-heating ability and removes pathogens with exoenzymes of therophiles at a temperature of 55° [2]. In order to provide an innovative guidance of wastewater treatment and engineering design, a laboratory-scale test of the ATAD for pre-treating abandoned strains of Klebsiella Pneumoniae is investigated and a new dynamic model is established with a showing temperature change.

Experimental

After the waste strains were concentrated by using a gravity thickening method, enzymatic kinetics of the ATAD was carried out at the facultative oxygen, in a batched-designed biochemical reactor with a main self-heating. In order to establish an exoenzymatic kinetic model of empirical Arrhenius-typed equation and avoid the existing equation shortcomings without the temperature changes and other factors, four factors related to reaction temperature, the TSS concentrations, aeration rate, and stirring rate were considered. Corresponding coefficients of the equation are obtained by ATAD test and the least squares regression. The temperature, aeration rate and stirring rate were adopted under 25 – 65 °C, 0.0919 – 0.1324 mL/s and 224 - 264 r/min, at the TSS feed concentration between 4.42 - 17.28 g/L, to maximize the TSS removal.

Results and discussion

From the respect of the engineering application, based on the analysis of feed TSS concentrations, TSS in raw waste-liquid was too low TSS concentrations to pre-treat by ATAD process. So, TSS in raw waste-liquid had to be concentrated before its treatment. After gravity thickening, the TSS concentration was 10.20 g/L, and the VSS concentration was 7.82 g/L, respectively. The results show that the TSS removal ratio was obtained up to 57.69% after more than 10th day under a maximum temperature of 65°. Comparatively, in order to obtain corresponding coefficients of the equation, logarithmic differential method is used to solve reaction orders of values of m, n, and q which correspond to the coefficients of TSS concentration, aeration rate and stirring rate.

The values of m, n, and q obtained were 1.579, -0.8175 and -0.6549, respectively. Under the experimental temperature, the apparent activation energy Ea was 6.8774 $kJ\cdot mol^{-1}$, pre-exponential factor k^0 was 7.1378 $(g\cdot L^{-1})^{-0.579}\cdot (ml\cdot s^{-1})^{0.8175}\cdot (r\cdot min^{-1})^{0.6549}$, and correlative coefficient of k^0 was 0.9223.

Deviation of the TSS removal efficiency predicted by the new model is validated with an actual test, with maximum relative deviation being 10.79%. Therefore, the innovative model has a good practicability.

Conclusions

The exoenzymatic kinetic model of empirical Arrhenius-typed equation is effectively set up by ATAD test for disposal of Klebsiella Pneumoniae strains. Correlative coefficient of pre-exponential factor is 0.9223, and theoretical relative deviation is 10.79% compared with a practical test. The innovative model can provide a theoretical guidance for wastewater treatment and engineering design as well.

References

[1]. Y. Lan, D. Jie, Z. Yu, Journal of Medicine of Chinese People's Liberation Army, 21(2003)69-70.

[2]. Zambrano, M. Gil-Martinez, M. Garcia-Sanz, Water Science & Technology, 60(2009)409-417.

PP-I-63

MODELING OF SELF-OSCILLATIONS IN CATALYTIC REACTIONS BY TWO-STAGE SCHEMES

Dimitrieva O.V., **Koltsov N.I.**

Chuvash State University, Cheboksary, Russia, E-mail: new_miracle@rambler.ru

It is known [1] that a two-stage scheme can not describe self-oscillations regimes of catalytic reactions taking place under isothermal conditions in the assumption of quasistationary on basic substances. In [2] shows the possibility of describing the self-oscillations of a two-stage schemes in non-isothermal conditions with constant concentrations of the main substances. In present paper is investigated the possibility of describing the self-oscillatory regimes in heterogeneous catalytic reactions of the two-stage schemes under isothermal conditions at changes of basic and intermediate substances concentrations.

The research based on a scheme known in the literature as a simple trigger [3]:

$$\begin{aligned} &Y_1 + Z = X, \\ &2Z + X = 3Z + Y_2. \end{aligned} \tag{1}$$

where Y_1 and Y_2 – basic substances, Z and X - free centers and centers filled by intermediate substances on the catalyst surface. Scheme (1) describes the system of ordinary differential equations

$$\begin{aligned} &\dot{z} = -(r_1 - r_{-1}) + (r_2 - r_{-2}), \\ &\dot{y}_1 = -(r_1 - r_{-1})p + (y_1^0 - y_1)q, \end{aligned} \tag{2}$$

where $r_1 = k_1 y_1 z,\ r_{-1} = k_{-1}x,\ r_2 = k_2 z^2 x,\ r_{-2} = k_{-2} y_2 z^3$ – rates of the first and second stages in the forward and reverse directions; y_1, y_2 – concentrations of basic Y_1 and Y_2 ($y_1 + y_2 = y_1^0 + y_2^0 = const$, y_i^0 – initial concentrations of the basic substances); z and x - concentrations of free Z and filled intermediates X centers on the catalyst surface ($x + z = 1$), $k_{\pm i}$ – rate constants of stages; $p = L / N$, $q = V / N$, V – velocity of gas flow in the reactor, N – number of molecules of the basic substances in the gas volume of the reactor, L – number of centers on the catalyst surface. Introducing dimensionless variables and parameters the system (2) is written in the form of the dimensionless model:

$$\begin{aligned} &\dot{u} = -m_1 uz - u + m_2 = f_1(z,u), \\ &\dot{z} = -uz + m_3 z^2 - z^3(m_4 - m_5 u) + m_6 = f_2(z,u), \end{aligned} \tag{3}$$

where $u = (k_1 y_1 + k_{-1})/q$, $\tau = qt$ – dimensionless concentration and time, $m_1 = k_1 p/q$,

$m_2 = (k_1\, y_1^0 + k_{-1} + k_1\, k_{-1}\, p/q)/q$, $m_3 = k_2/q$, $m_4 = (k_2 + k_{-2}(\, y_1^0 + k_{-1}/k_1 + y_2^0\,))/q$, $m_5 = k_{-2}/k_1$, $m_6 = k_{-1}/q$ – dimensionless parameters. In model (3) all parameters are positive. System (3) corresponds to the characteristic polynomial of second degree

$$\lambda^2 + \sigma_1 \lambda + \sigma_2 = 0\,. \tag{4}$$

Based on method of analysis of the coefficients of the characteristic polynomial (4) found the fields of system parameters (3) with different types of dynamic behavior. In particular field of existence of self-oscillatory regimes are defined. Fig. 1 shows the results of calculating the trajectories of changes in the concentrations of intermediate z and basic u substances over time (profiles $z\ (t)$ and $u\ (t)$ in the environment of the steady state (z_∞=0,3270698, u_∞=2628,001501)) for values of the parameters m_1 = 0,02, m_2 = 2645,1923, m_3 = 8000, m_4 = 34394,393, m_5 = 10, m_6 = 287,65.

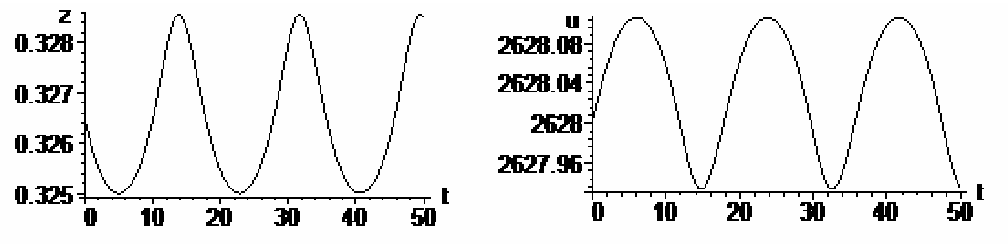


Fig. 1. Profiles $z\ (t)$ and $u(t)$: $z(0)$= 0,32647, $u(0)$= 2628,001

Thus the account of change of concentration as the basic and intermediate substances allows to describe isothermal self-oscillations of catalytic reactions by the simple two-stage scheme (1).

References

[1]. Koltsov N.I. Mathematical modeling of catalytic reactions. Cheboksary, **2007**, 294.

[2]. Bykov V.I., Tsybenova C.B. Russ. J. Phys. Chem., **2009**, Vol. 83, N 4, 709-718.

[3]. Yablonsky G.S., Bykov V.I., Elokhin V.I. Kinetics of model reactions of heterogeneous catalysis. Novosibirsk, **1984**, 223.

Acknowledgements

Possibility of describing the self-oscillatory regimes in heterogeneous catalytic reactions of the two-stage schemes under isothermal conditions at changes of basic and intermediate substances concentrations is shown.

PP-I-64

PROBLEMS OF DIVISION OF ISOTOPES OF LUNGS AND AVERAGE ELEMENTS A METHOD OF A CHEMICAL ISOTOPE INTERCHANGE

Dauletbai A.D.[1], Myrzaliyeva S.K.[2]

[1]"National Center on Complex Processing of Mineral Raw Materials of the Republic of Kazakhstan" RSE, 67 Zhandosov str., Almaty, the Republic of Kazakhstan,
dauletbai-aizhan@mail.ru
[2]Almaty State University, 100 Tole bi str., Almaty, the Republic of Kazakhstan,
saulekerchaiz@mail.ru

Chemical methods of division of isotopes have found in many cases successful practical application and the basic theoretical questions connected with use of these methods, are developed.

In system from two substances which are not chemically co-operated with each other, reaction of isotope interchange may take place with a constant of balance distinguishing from value, corresponding to equally probable distribution of isotopes between molecules participating in reaction. Division of isotopes by a method of a chemical interchange is based on such reactions.

Coefficient of separation of isotopes (α) lungs and average elements inevitably should differ from unit and consequently the question of possibility of division almost coincides with a problem of search of optimum systems for division of isotopes of these elements. Not optimum systems with reference to average elements not enough prospects.

Applicability of this or that system for division of isotopes is defined first of all by its two characteristics: in size of coefficient of separation of isotopes (α) and speed of course of reaction of an isotope interchange.

Size of coefficient of separation which is taking place at reaction of an isotope interchange between two any connections of the given element, are defined as the relation so-called β - factors of these connections:

$$\alpha = \beta_1 / \beta_2$$

β - factors are unequivocally connected with relations of the sums on conditions of isotope forms of connections, and, hence, they characterise in the exhaustive image thermodynamic possibilities of connections concerning division of isotopes.

We calculate and investigate perspective systems, suitable for practical division of isotopes of some elements.

POSTER PRESENTATIONS

SECTION II

COMPUTER OPTIMIZATION OF OXIDIZING TRANSFORMATION PROCESS OF METHANOL INTO FORMIC ACID IN PRESENCE OF MODIFIED ZEOLITE CATALYSTS

Aliyev A.M., Majidova S.M., Aliyev Q.S., Mamedov E.M., Huseynov K.A.

Institute of chemical problems, Azerbaijan Republic, Baku
E-mail: chemproblem@mail.ru

In the report results of graphical and parametrical optimization of obtaining process of formic acid by oxidation of methanol on modified zeolite catalyst Pd-mordenite will be presented.

Researches on studying of kinetic laws of the process, the developed kinetic model and specification of its regime parameters have been carried out.

With application of the personal computer and the created software the graphics allowing visually to observe character of change of output products have been obtained and to define optimum routes of process course.

For realization of parametrical optimization as criterion the output of formic acid was accepted. Problem of optimization of oxidising transformation of methanol into formic acid on Pd-containing zeolite the catalyst it is formulated on the basis of kinetic model:

$$r_{CHOOH} = k_1 P_{O_2} \left\{ \frac{\sqrt{1 - 4\left(\frac{k_1 P_{O_2}}{k_2 P_{CH_3OH}} + \frac{k_1 P_{O_2}}{k_3}\right)\left(\frac{k_2}{k_4} P_{CH_3OH} - 1\right)} - 1}{2\left(\frac{k_1 P_{O_2}}{k_2 P_{CH_3OH}} + \frac{k_1 P_{O_2}}{k_3}\right)} \right\}^2 ,$$

$$r_{CH_2O} = \frac{k_5 K_1 K_2 P_{O_2} P_{CH_3OH}}{\left(1 + K_1 P_{O_2} + K_2 P_{CH_3OH}\right)^2} ,$$

$$r_{CO_2} = \frac{k_6 K_3 K_4 P_{O_2} P_{CH_2O}}{\left(1 + K_3 P_{O_2} + K_4 P_{CH_2O}\right)^2} ,$$

where r – speed of stages corresponding to index, P_{O_2} and P_{CH_3OH} – partial pressures of components corresponding to index, k_1, k_2, k_3, k_4 – constants of speeds of stages corresponding to index, K_1, K_2, K_3, K_4 – constants of adsorbsion balance, to find such values of operating parameters (temperature of a reactionary zone - T, mol ratio methanol : oxygen : nitrogen, partial pressures P_{O_2} and P_{CH_3OH}, volume speed – V) at which the maximum output of formic acid - A is reached.

$$\max\ A\ (T, V,\ P_{O_2},\ P_{CH_3OH})$$

At the following restrictions on technological parameters

$$85 \le T \le 125^0 C; \quad 900 \le V \le 3200\, h^{-1}; \quad 0{,}13 \le P_{0_2} \le 0{,}6\, atm; \quad 0{,}09 \le P_{CH_3OH} \le 0{,}43\, atm$$

On results of the obtained graphics and calculations of regime parameters the following data have been obtained: the maximum value of output of formic acid - A is equal to 43,8 % and it is reached at following values of operating parameters:

Temperature of a reactionary zone - T = 115 °C; volume speed - V = 1500 h^{-1}; partial pressures - P_{O_2} = 0,26 atm and P_{CH_2O} = 0,21 atm; mol ratio CH_3OH:O_2:N_2 – 1:1:2

Results of calculations can be applied for optimum projecting of oxidising transformation process of methyl alcohol into formic acid on modified natural mordenite.

PP-II-2

MATHEMATICAL SIMULATION OF SOLID PHASE NANOREACTOR EFFECT IN THE NETWORK POLYMERS BASED ON CALIX[4]RESORCINARENE

Altshuler H.N.[1], **Altshuler O.H.[2]**

[1]*Kemerovo division of Institute of Solid State Chemistry and Mechanochemistry SB RAS, Kemerovo, Russia, sorbent@kemnet.ru*
[2]*Kemerovo State University, Kemerovo, Russia*

The cup of bifunctional cis-calixarene (Fig. 1) acts as nanoreactor. In works [1], [2] network polymers based on cis-calix[4]resorcinarene for the first time are used as matrixes to create solid phase nanoreactors for catalytic hydrogenation.

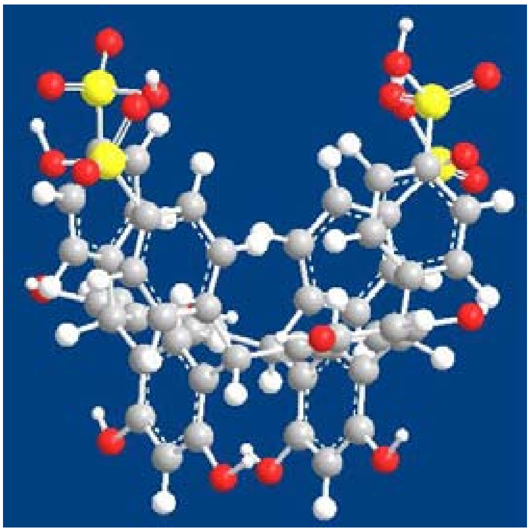


Fig. 1. Cis–tetrasulfonatophenylcalyx[4]resorcinarene structure minimized in terms of enthalpy of formation by the semiempirical PM6 method within the MOPAC 2009 program.

In this work it is shown that interaction of the network functionalized polymers based on *cis*-calix[4]arene with aqua solutions of electrolytes is determined by ion exchange controlled by diffusion of ions in a polymeric phase.

The nanoreactor effect consisting in hundredfold increasing of cation diffusion flux in bifunctionalized polymers containing sulfonate and phenol hydroxyl ionogenic groups was found. For steady and non-steady states the solutions of the fundamental differential equation of cation diffusion in functionalized polymers by means of the model of a spherical layer are obtained for a variety of initial and boundary conditions provided the diffusion coefficient is constant. For non-steady state degree of transformation *F* in time *t* is

$$F = \frac{\left[\left(b^2 + \frac{ab}{2}\right) - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\left\{b^2 - ab\cos n\pi\right\}\frac{\exp\left\{-Dn^2\pi^2 t/(b-a)^2\right\}}{n^2}\right]}{a^2 + ab + b^2},$$

where *a* and *b* –distances from the center to the inner or outer surfaces of a spherical layer of the polymer granule, *D* – interdiffusion coefficient.

Graphs of *F* against $\left(Dt/(b-a)^2\right)^{1/2}$ are shown in Fig. 2 for different values of *b*/*a*.

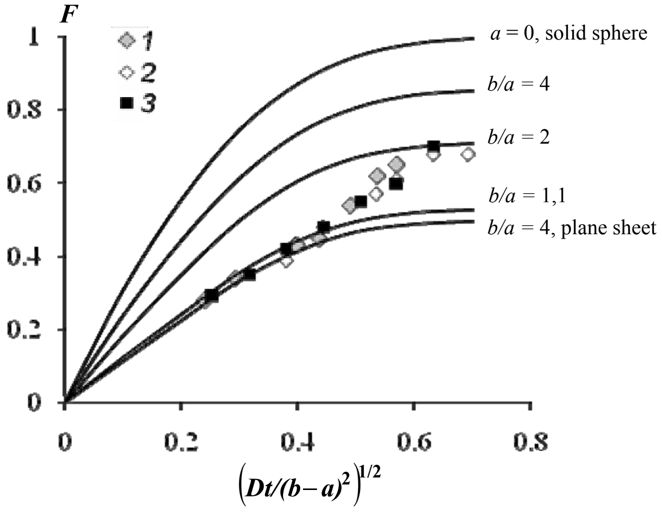


Fig. 2. Dependence *F* from $\left(Dt/(b-a)^2\right)^{1/2}$. Curves - calculation; dots - experiment: *1* - cation sorption from 0.1 mol/dm^3 NaOH solutions; *2* - cation sorption from 0.03 mol/dm^3 NaOH solutions; *3* - cation sorption from 0.05 mol/dm^3 LiOH solutions by sulfonated polymer.

The proposed mathematical model explains the nanoreactor effect in polymers based on cis -tetraphenyl calyx[4]resorcinarene and predicts considerable improvement of the kinetic characteristics of cation exchangers containing weakly dissociating ionogenic groups upon introducing into them strongly acidic functional groups.

References

[1]. H. Al'tshuler, L. Sapozhnikova, Synthesis of Ultradisperse Transitive Metals in Immobilized Microreactors, Journal of structural chemistry, **2004**, Vol. 45, Supplement, P. 178-182.

[2]. H. Al'tshuler, L. Sapozhnikova, Preparation of Ultradispersed Transition Metals in Immobilized Microreactors, Russian Journal of Applied Chemistry, **2004**, Vol. 77 (Issue 11), P. 1896-1898.

PP-II-3

INVESTIGATION OF CONCURRENT PROCESSES OF HEAT EXCHANGE AND CHEMICAL TRANSFORMATION IN CASCADE REACTORS WHEN SYNTHESIZING BUTADIENE RUBBER ON COBALT AND NEODYMIUM- CONTAINING CATALYST SYSTEMS

Aminova G.A., Ignashina T.V., Manujko G.V., Diakonov G.S.

The Kazan state technological university, Kazan, Russia, a_guzel@mail.ru

Maintaining of necessary temperature in reactors of the cascade in process solution polymerizations will reduce in deriving rubber with controllable molecular-mass performances and, as a corollary, with the given processing behavior. With the purpose of investigation examination of influence of operating temperature of an industrial run on molecular-mass performances of polymer the generalized models of the combined processes of chemical transformation and heat exchange was developed designed at deriving rubber SKDN and SKDK. On the basis of received models optimal operating conditions were defined.

The quantitative theory for calculation of average molecular weights and molecular-mass distributions of the polymers have designed which are nascent in processes, complicated by chain transfer reactions and cross growth, at deriving butadiene rubber on a cobalt and neodymium- containing catalyst systems. The most important regularities of shaping of molecular-mass performances of polymer in continuous processes were defined. Complete analysis of fields of a concentration distribution, velocities and temperatures inside a polymerized for detection of reasons of uncontrollable widening of molecular-mass distribution (MMD), bimodality MMD was carried out, etc. Examination of the combined processes of heat exchange and chemical transformation in reactors of the cascade was carried out, dependences of molecular-mass performances of polymer on the basic operation condition regime parameters of process (residence time, temperature, concentration of initial reagents, an amount of reactors in the cascade) was established.

HONEYCOMB MONOLITHIC CATALYST REACTORS FOR SPACE PROPULSION APPLICATIONS

Amrousse R.*, **Farhat K.**, **Batonneau Y.** and **Kappenstein C.**

LACCO (Laboratoire de Catalyse en chimie Organique), Poitiers 86022, France
**Corresponding author: rachid.amrousse@univ-poitiers.fr*

The pellet and the grain catalysts have been widely used in space propulsion applications, such as launcher, satellites and gas generator (e.g. rescue systems) [1, 2]. The use of monolith in these applications is only at the development stage. However, compared to conventional catalysts shape (e.g. pellets, spheres, grains), monolithic catalysts have several advantages such as (i) low pressure drop, (ii) possibility of using high flow rate, (iii) easiness in scale-up and in some cases (iv) selectivity enhancement. Nevertheless, this type of materials presents a very low surface area, and therefore needs the deposition of a secondary porous support in the form of a washcoat layer.

In our laboratory we are also interested by the development of the wash-coating phase in order to increase the surface area of the monolithic support and therefore the metallic active phase(s). In the present work, honeycomb-based catalysts have been manufactured from ceramic monoliths containing porous γ-alumina as a secondary support. This later has been prepared from boehmite colloidal suspension and urea, and deposited onto the internal surface of the monolith. The active phase components are based on precious metals (Pt, Ir or Rh) or transition metal oxides such as MnO_2 [3].

To follow the catalytic activity, cordierite-based honeycomb catalysts ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) (Figure 1) were evaluated for the decomposition of energetic compounds such as hydrogen peroxide, hydroxylammonium nitrate, ammonium dinitramide, ignition of cold $H_2 + O_2$ mixtures.

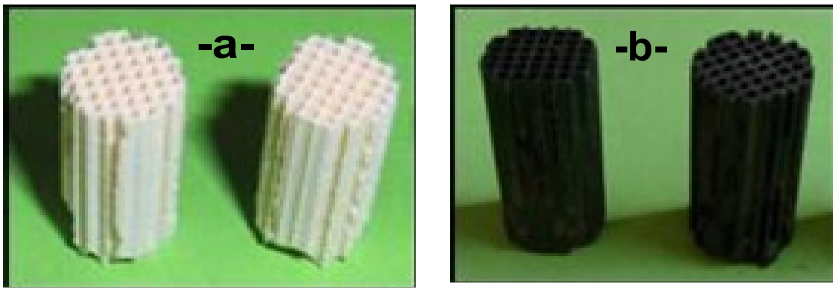


Fig 1. The as-received monoliths (1 cm in diameter) (a) and the catalysts after wash-coating by porous alumina and impregnation by iridium (b).

The control of the catalytic bed and the different preparation key parameters of the catalysts remain an important way to improve the catalytic decomposition and the catalytic ignition performances: (i) honeycomb-type ceramic monoliths, (ii) wash-coating procedure, (iii) impregnation steps: the active phase is deposited inside the porosity of the coating layer by impregnation of the active phase precursor followed by drying, calcination and/or reduction. The monolithic catalysts based on the noble metals are characterized by different physico-chemical techniques to understand their behavior.

References

[1]. R.W. Humble, G.N. Henry, W.J. Larson, Space propulsion analysis and design, MacGraw-Hill,New-York, 1995.

[2]. Y. Batonneau, C. Kappenstein, and W. Keim, "Catalytic decomposition of energetic compounds: gas generator, propulsion", in Handbook of Heterogeneous Catalysis, G. Ertl, H. Knözinger, F. Schüth, and J. Weitkamp Eds, Vol. 5,Chapter 12.7, VCh-Wiley, Weinheim, Germany, 2008, pp. 2647-2676.

[3]. E.M. Johansson, D. Papadias, P.O. Thevenin, A.G. Ersson, R. Gabrielsson, P.G. Menon, P.H. Björnbom, S.G. Järas, Catalytic Combustion for Gas Turbine Applications, Catalysis, vol. 14, The Royal Society of Chemistry, Cambridge, 1999, pp. 183–235.

Acknowledgements

The authors thank the French Spatial Agency (CNES) (Centre national d’Études Spatiales, Evry, France) for the finantial support.

MATHEMATICAL MODELING OF THE ALUMINA POWDER SYNTHESIS BY PLASMA CHEMICAL PROCESSES

Arkhipov V.A.[1], **Zhukov A.S.**[2]

[1]Research Institute of Applied Mathematics and Mechanics
of Tomsk State University, 634050, Tomsk, Russia
[2]Tomsk State University, 634050, Tomsk, Russia
leva@niipmm.tsu.ru

Jet plasma processes (spray pyrolysis) are the universal high productive methods to obtain ceramic powders of various content and shape sizes [1]. The actual problem being considered in the report that provides the efficiency of plasma chemical processes as methods to obtain alumina powders is to determine control parameters and their effect on the content, properties, structure and shape sizes of the powders being obtained.

During spray pyrolysis the solution $Al(NO_3)_3{\cdot}9H_2O$ is atomized into reactor, where the aerosol droplets undergo evaporation and solute condensation within the droplet, drying, thermolysis of the precipitate particle at higher temperature to form a microporous particle, and, finally, sintering of the microporous particle to form a dense particle.

To obtain the spraying parameters, we studied the flow rate characteristics and the geometry of the spray cone of the centrifugal injector used in the swirl reactor considered. To determine the aerodynamic and thermodynamic characteristics of the spray cone, we have to consider the flow field with two phases and take into account momentum, mass, and heat transfer between the phases. The problem of calculating the local characteristics of the flow in the swirl-reactor spray cone was considered in a similar manner [2].

The equations of motion for the gas phase were written in the Euler form under the assumption of insignificant influence of local discontinuities in the flow, caused by the presence of droplets in the gas phase. The equations of motion in the Lagrangian form, the equation for the change in the droplet radius due to vaporization, and the heat-balance equation were written for droplets of finite number of fractions. Interaction between the phases was taken into account by considering droplets as internal sources for gas phase. In this case, the right side of equations that describe the gas phase behavior was supplemented by additional terms caused by interaction of droplets with the gas medium.

The turbulence characteristics were calculated on the basis of a two-parameter model with the use of balance equations for the turbulent kinetic energy and the rate of its dissipations.

For each fraction of droplets, the equations of conservation of momentum were written. The drag law was defined by Klyachko's formula [3]. To calculate the droplets trajectories, we supplemented the above-given system by the kinematics relations.

The equations for the gas phase were solved numerically by the finite-volume method [4]. In accordance with this method, the finite-difference equations were derived by integrating the differential equations over the control volumes containing nodes of the finite-difference grid. Equations for liquid phase were integrated by fourth-order Runge-Kutta method.

The closed physicomathematical model and results of numerical study of spray pyrolysis synthesis being presented in the report permit to determine the morphology and size distribution function of alumina particles.

This work was carried out within the framework of realization of the Federal target program "The Scientific and scientific-pedagogical staff of innovative Russia" for 2009–2013 with a support of State contract from 04.08.2009 "Developing and processing of the high-energy filled polymer compositions".

References

[1]. G.L. Messing, S.-C. Zhang and C.V. Jayanthi. Ceramic Powder Synthesis by Spray Pyrolysis // J. Am. Ceram. Soc. 1993. Vol. 76, No 11. – p.p. 2207–2726.

[2]. V.A. Arkhipov, O.V. Matvienko, and V.F. Trofimov. Combustion of Sprayed Liquid Fuel in a Swirl Flow // Combustion, Explosion, and Shock Waves. 2005. Vol. 41, No 2. – p.p. 140-150.

[3]. L.S. Klyachko. Equation of Motion of Dust Particles in Dust Traps // Otoplen. Ventil. 1983. № 4. – p.p. 27–29.

[4]. S.V. Patankar. Numerical Heat Transfer and Fluid Flow, MacGraw Hill, New-York, 1980.

MODELING OF VINYL ACETATE SYNTHESIS FROM ACETYLENE AND ACETIC ACID

Avetisov A.K.

Karpov Institute of Physical Chemistry, Moscow, Russia, avetisov@cc.nifhi.ac.ru

The vapor phase synthesis of vinyl acetate according to

$$C_2H_2 + CH_3COOH \; = \; CH_2{=}CHOCOCH_3 \qquad (A)$$

usually is performed in a reactor with the fluidized bed of a catalyst (zinc acetate on activated carbon) in mixtures with excess of acetylene (C_2H_2: CH_3COOH = 4 ÷10) at 160-230°C, pressures close to the atmospheric one, and at acetic acid conversions about 30%. In order to compensate continuous deactivation of the catalyst and its partial loss, one continuously increases the temperature in the reactor in such a way that the total capacity of the unit remains constant. After limiting (with respect to the catalyst thermal stability) temperature (230°C) is reached, the process is terminated, and the catalyst is replaced by a new one.

The object of the present work is to find a theoretically optimum mode (initial temperature of the process and rate of its elevation, i.e. the unit capacity and cycle time) which should meet the maximum surplus criterion.

The kinetics of reaction (A) is described by the equation:

$$r = \frac{kP_1P_2}{1 + b_1P_2(1 + b_2P_2)}, \qquad (1)$$

where k, b_1 and b_2 are constants, P_1 and P_2 are partial pressures of acetylene and acetic acid, respectively.

Under conditions of commercial process (almost constant P_1, denominator close to unity) equation (1) transforms into

$$r = kP_1 = k' \qquad (2)$$

It was established experimentally, that the catalyst is deactivated according to the following kinetics

$$r_d = k_d \frac{P_2}{P_1} a^2 = k_d^0 \exp(-A_d / T) \frac{P_2}{P_1} a^2 = -\frac{da}{dt}, \qquad (3)$$

where a is the catalyst activity which represents the ratio of the reaction rate at the start of the process and at time t. It is supposed that the catalyst loss is described by the equation

$$-\frac{dv}{dt} = k_l\left(v - v_f\right), \tag{4}$$

where k_l is the catalyst carry-over, v_f is the remaining part of the catalyst by the end of the process.

For a pseudo zero-order reaction, the reactor capacity is equal to the reaction rate:

$$G = kaVv = k^0\, exp(-A/T)aVv\,, \tag{5}$$

where G is the unit-per-hour productivity, V is the initial catalyst load in the rector, A = E/R, E is the activation energy.

From here it follows

$$T = \frac{A}{ln\,k^0 + ln\,a + lnV - lnG}\,. \tag{6}$$

Substituting expression (6) into (3) and integrating, one obtains

$$a = \left[(m-1)k^{*}t + 1\right]^{1/1-m} \text{ if } m \neq 1 \text{ and } a = exp(-k^{*}t) \text{ if } m = 1\,. \tag{7}$$

In equation (7) $m = 2 - A_d/A$, $k^{*} = k_d\left(k^0/G\right)^{-A_d/A} P_2/P_1$,

The integration of equation (5) gives

$$v = v_f + \left(1 - v_f\right)exp(-k_l t) \tag{8}$$

After substituting expression (7) and (8) into (6), one obtains function $T=f(t)$ under the constant G.

From condition maxima $\frac{dR}{dG}$ (where profit $R = \dfrac{\beta_1 \int_0^{t_f} Gdt - \beta_2 \int_0^{t_f+t_c} dt - \beta_3 - \beta_4}{t + t_c}$

β_1 – difference between price of vinyl acetate and acetylene and acetic acid , β_2 и β_3 – semi-variable and semi-fixed costs, respectively, β_4 – price of catalysis loading, t_f – process duration, t_c – reloading catalysis duration) the theoretical optimal productivity was estimated.

CENTRIFUGAL DISK REACTOR

Avvakumov Evgeny

Institute of Solid State Chemistry and Mechanochemistry of Siberian Branch of RAS
avvakumov@solid.nsc.ru

The design of milling centrifugal machines has significantly in recent years. The hard mechanical action in these machines is provided by centfifugal forces which appears during interaction of high-speed revolving disks inter wall of hull. In proposed new constuction of centrifugal disk reactor (fig.1), the milling device is placed inside reactor [1].

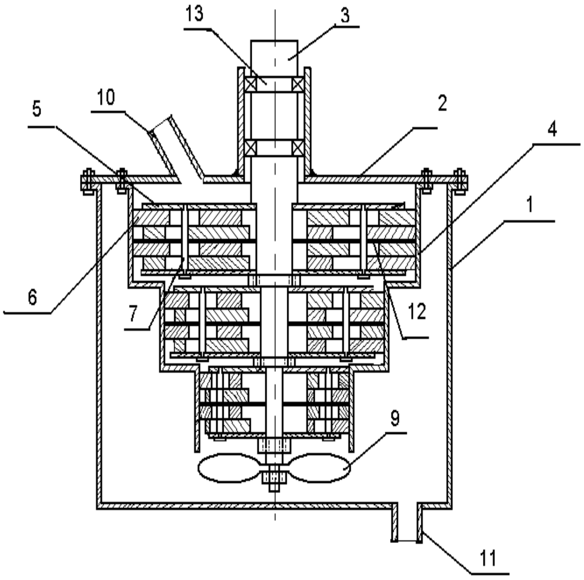


Fig.1. Centrifugal disk reactor.

1 – hull of reactor, 2 – lid of reactor hull, 3 – driving shaft, 4 – hull of milling device, 5 –nestle plates for disk shaft, 6 – disks, 7 – shaft for disks, 9 – blade, 10 – inlet, 11 – outlet, 12 – partition, 13 –bearings.

The effective mechanical treatment is provided by using of disks of two types: disks with central apertures for shaft and disks with apertures displacing from center disk. In this reactor the efficiency of milling and mechanical activation increases in 2-3 times in comparison with the reactor which has disks with only central apertures. The circulation of treatment materials (suspensions) is provided by blade 9 and the apertures on upper part of milling device (on fig.1 not shown).

References

[1] Patent 2367514 RF. C1 B01J 19/18. Centrifugal disk reactor.Bull. of inventions.№26. 20.09.2009

PP-II-8

THE TUBULAR CATALYTIC REACTOR WITH INTERCHANGEABLE CHAMBER AND THE MULTIZONED CONTROLLER OF THE LONGITUDINAL TEMPERATURE PROFILE

Bachurikhin A.L.

Zelinsky N.D. Institute of Organic Chemistry of the Russian Academy of Science,
Russia, Moscow 119991, GSP - 1, the Leninscky av., 47,
E-mail: SECRETARY@ioc.ac.ru

Now on a share of catalytic processes the basic part of world volume of production of petrochemical and organic synthesis is necessary. The special role, first of all in sphere of oil refining is allocated to a class of the processes sold with participation of heterogeneous catalysts. In turn, the significant part such processes is realized with application of tubular reactors with a fixed bed of the catalyst. For the present moment there is a huge quantity of design decisions and the executions of reactors of such type dependent on type of processes, conditions and catalysts in which they are used **[1-4]**. Nevertheless, as always it happens in the field of designing the new equipment, practically any model the reactor equipment is characterized not only advantages, but also concrete lacks. In our opinion, now there are no models of flowing tubular reactors with which help it is possible to provide to the full such function advantages, as fast and convenient the catalyst replacement, change of a direction of modes of feeding of initial products and removals of products of reactions without a stop of process, and also an opportunity of the operative control and recustomizing longitudinal temperature a profile of reactors.

In connection with the specified lacks works on search of corresponding design decisions have been initiated, the skilled model of a flowing tubular reactor with displacement volume of the catalyst 50L is developed and made. The reactor differs the following features:

1) An opportunity of fast replacement of work chamber of the catalyst in connection with dissociation this chamber and a thermostat providing regulation of temperatures

2) An opportunity of operative change of dimensional orientation of a reactor between horizontal and vertical positions without a stop of technological processes that allows to provide ascending, descending and horizontal modes of feeding of initial products

3) An opportunity of operative regulation longitudinal temperature a profile of a reactor and maintenance of construction of isothermal, falling and growing dependences of temperature along length of a reactor.

Characteristics of a reactor:

1) Operating temperatures — Up to 900°C
2) Producing pressures — 0÷10MПа
3) Integral capacity of heaters — Up to 20KWt
4) Quantity of controlled zones heating — Up to 10
5) A maximal longitudinal gradient of temperatures — 500°C/м
6) Weight in assembly — No more than 0,3 tons
7) Dimensions — 3×0,7×0,7 m

The basic constructional material of building bag and thermostat is stainless steel AISI 321. As a material of a heat insulation the bed soft silica fibres with contents SiO_2 of 96 weights of %, the rest Al_2O_3 is used. The task and adjustment longitudinal temperature a profile is controlled with the help of heat regulators - Thermodat, developed by Open Company "MONITORING SYSTEM" Perm, the Russian Federation.

The basic range of application of a reactor — the majority of catalytic transfomations of petroleum hydrocarbons and gas, and also the processes of organic synthesis proceeding with use of heterogeneous catalysts in a fixed bed. The reactor has passed successful pilot tests during catalytic transformation of a debutanized gas condensate in a concentrate of aromatic hydrocarbons with the contents of fraction BTX (Benzene, Toluene and Xylenes) up to 50 weights of %, and also partial oxidation of natural gas in methanol and other oxychemicals. The generated sample of a reactor passes a stage of reception of the patent for useful model.

References

[1]. Patent Japan., 2001087644, Catalytic reaction apparatus and reforming apparatus with same., Inv. Mizobuchi, Manabu, etc.
[2]. Patent Japan., 2002095959, Reaction container having temperature control for temperature gradient., Inv. Kondo, Seiji, etc.
[3]. Patent Japan., 2002128503, Catalytic reactor with catalyst temperature control., Inv. Miyoshi, Kazuo, etc.
[4]. Patent Japan., 2004305942, Catalytic reactor and fuel reforming system and fuel cell system., Inv. Waki, Norihisa.

NEW STRUCTURE OF THE PLATINOID CATALYTIC GAUZES FOR AMMONIA CONVERSION REACTORS USED FOR PRODUCTION OF NITRIC ACID AND MINERAL FERTILIZERS

Barelko V.V.*, Bykov L.A., Ivanyuk A.G.***,**
Chepelenko V.N.*, Shults V.A.****, Bogidaev R.Yu.******

**IPCP RAS, Chernogolovka; **CHEMPHYST limited company, Chernogolovka;*
****MZSS, Moscow; ****JSC AKRON, Nizhniy Novgorod*

New-generation platinoid catalytic gauzes for ammonia conversion have been developed to be used for production of nitric acid and mineral fertilizers, hydrocyanic acid, nitrites and nitrates, and in other processes comprising the step of catalytic oxidation of ammonia to nitrogen oxides.

New properties of proposed catalytic material

Geometrical and composition structure of proposed catalytic gauzes platinoid materials and the method for the formation of catalytic package are different from those used for systems in national and world practice (a square cell, weaving density is 1024 knots/cm^2) as a result of the use of nonsymmetrical scheme of wire interweaving and a new combination of materials. Such changes in geometrical and structural parameters of grids provide higher product output from a gauze mass unit, higher ammonia conversion to nitrogen oxides, lower (by 20-40%) weight of a platinoid catalytic package. A physical reason of achieving the above technological effect consists in that the proposed catalytic gauzes are characterized by lower diffusion resistance in the process of ammonia conversion and lower density of wire interweaving (ballast zones on a catalytic gauze).

Comparative characteristics

The main results of pilot and industrial tests realized during conversion ammonia in UKL-reactor:

Technological parameters	**Conventional catalysts (Alloy 5, 32x32 wires per cm, wire thickness is 0.092 mm)**	**Catalysts of new geometry of weaving (wire thickness is 0.092 mm)**
A number of layers in a package	12	10
Mass of platinoid in a package (a.u.)	1	0,72
Ammonia conversion	93%	96-97%

Level of novelty of the development and proposed technology

[1]. Russian patent No 2002131702 от 26.11.2002 “Platinoid catalyst as a wire gauze”

[2]. Application for an international patent No PCT/RU2003/000527 of the 26th November 2003 “Platinoid catalyst in the form of a wire gauze”.

UV-ACTIVATION OF METHANE COUPLING IN THE MEMBRANE REACTOR

Basov N., Oreshkin I., Tereshchenko G.†, Ermilova M., Orekhova N.

A.V. Topchiev Institute of Petrochemical Synthesis of RAS, Moscow,
Russian Federation, basov@ips.ac.ru

The methane conversion to hydrocarbon C_2 and above (the methane coupling) is of interest because it may allow to consider the natural gas, as alternative to oils as the source of these compounds. The basic temporary methods to produce hydrocarbon C_2 and above from methane is a thermal activation of the CH_4 molecules that breaks C-H bond. This is possible under catalytic dehydrogenation, for instance, on metals of the platinum group. However, high temperature of the process brings about an uncontrolled breakup of the bonds in the methane molecule with free carbon formation. It is known that the energy required for a take off of the hydrogen atom from the methane molecule is equal 435.4 kJ/mol [1]. In recalculation on one molecule this energy corresponds to energy saturation of ultraviolet radiation. To use the ultraviolet activation allows to conduct the process under low temperature, but because of reversibility of the reactions the methane conversion remains low.

The aim of this work was to determine the possibility of the methane coupling in a reactor with palladium alloy membrane and activation of the CH_4 molecules by the energy of the UV-radiations with the different types of mercury lamps. The low pressure mercury lamps produce more hard UV radiation than the high pressure mercury lamps, but under practical realization have shown low efficiency because of small intensity of the luminescence. The Significant results were obtained with using the high pressure mercury lamps.

Optimum radiant energy of the source use providing possibility of the reactor temperature control without loss of radiating abilities of the mercury lamp under its cooling, was received under mutual location of the optical quartz glass reactor and lamp on the axises of the elliptical cylinder. Its shining metal surface reflected and condensed the UV-beams in the inner reactor space. Placed inside a reactor the palladium alloy membrane allowed not only to catalyse reaction, but also to shift chemical equilibrium due to the removing evolved in reaction hydrogen from reactionary space.

The experiments were provided under atmospheric pressure of the pure methane (99.99%) in temperature interval 475 – 525 K. The tube from the alloy of palladium with 5 mass.% of ruthenium was placed inside the reactor. The length of a tube was 1 m, with diameter 1 mm and wall thickness 0.05 mm. The results have shown the possibility of the realization non oxidative methane coupling with non thermic activation of CH_4 molecules.

The maximum methane conversion was obtained when through the palladium alloy tube, placed inside a reactor filled by methane, was given argon flow, by means of which hydrogen moved from the reaction zone, where it was formed as the result of methane coupling. So the methane conversion under the temperature 430 K increased from 1.3 %, obtained under the same temperature without hydrogen removing, to 5.2 % when hydrogen was removing through a membrane catalyst (Table 1). The main of the reaction products was propane and ethane with small quantity of the ethylene, identified at conversion above 1%.

Table 1. **The methane conversion and the composition reaction products**

Time from the beginning, h	Without H_2 removing				With H_2 removing			
	Conversion, %	C_2H_4, %	C_2H_6, %	C_3H_8, %	Conversion, %	C_2H_4, %	C_2H_6, %	C_3H_8, %
2	0.44	trace	0.1	0.34	0.93	0.02	0.19	0.72
4	1.01	trace	0.22	0.79	2.52	0.14	0.56	1.82
6	1.16	trace	0.45	0.71	4.64	0.3	1.12	3.22
6.25	1.27	trace	0.41	0.86	-	-	-	-
8	-	-	-	-	5.29	0.44	1.34	3.51

References

[1]. V.S. Arutyunov, O.V. Krylov. Okislitel'nye prevrashchenia metana. P.5. «Nauka», M, 1998

Acknowledgements

The financial support of this work was conducted within the framework of the program "CHEMICAL ASPECTS of ENERGY" of Prezidium of Russian Academy of Sciences

COMBINED APPROACH (FMEA- HAZOP-TABLE KARNAUGH) FOR RISK ANALYSIS RELATED TO A CHEMICAL PROCESS

Benamrane B.*, **Bourmada N.***, **Chetouani Y.****

**National Institute for Occupational Health and Safety, University of BATNA ALGERIA,*
Laboratory analysis of occupational hazards and industrial LARPI,
benambad@ yahoo.fr
***Department of Chemical Engineering University of Rouen France*

Seveso, Bhopal, Toulouse, are so much accident which by their destructive potential made conscience in opinion for the problems of risks generated by industrial process. We offer in this paper a methodology of analysis of inherent risks in the functioning of a chemical reactor, we shall note that accident can be caused either by a fault in the functioning of the reactor, or by the drift of a parameter of chemical reaction. We opt for HAZOP method for the analysis of risk generated by chemical reaction, while FMEA method will be chosen to be the analysis of risks linked to the functioning of the chemical reactor. However, we note the existence of an interaction between the course of chemical reaction and behavior of the reactor this leads us to develop a new analytical approach to this specific type of system, wich based on the combination methods (FMEA – HAZOP - TABLE KARNAUGH). This combination is obtained using the method table KARNAUGH. The most feared risk in our system is the risk of thermal runaway, then we base our study on various faults leading to the risk of runaway in both subsystems. This approach allows us to simplify our study by incorporating the faults seen in the same context, and especially by highlighting the various interactions between the two subsystems. We obtain a simple final electrical schematic and a simple equation that describes the occurrence of different scenarios of thermal runaway in chemical processes.

Keywords: Chemical process, thermal runaway, FMEA, HAZOP, TABLE OF KARNAUGH.

VIBRATING MULTIFUNCTIONAL CHEMICAL REACTORS FOR SMALL-SCALE CHEMICAL AND PHARMACEUTICAL PRODUCTION

Chistovalov S.M.

A.N. Nesmeyanov Institute of organoelement compouns RAS (INEOS RAS)
119991 Moscow, V-334, GSP-1, Vavilov str., 28
Tel: 7(499)1358298, fax: 7(499) 1355085, E-mail: sm53@ineos.ac.ru

Development of essentially new chemical reactors is a question of vital importance for all areas of small-scale chemistry and first of all for production of substances of synthetic medical products. Creation of the multifunctional chemical reactors, where the gas heat-carrier is not used, without mixing devices and seals in the working volume, without stagnant and difficultly washed out zones is one of ways for improvement of quality and purity of an obtaining product, maintenance of profitability and ecological safety of manufacturing small-scale chemistry. Only such the multifunctional equipment, allowing to carry out all technological process in one volume, will enable to create on their base flexible chemical engineering systems (FCES), capable without realignment and with high efficiency to make the wide nomenclature of products [1,2].

We have developed the vibrating multifunctional chemical reactor, allowing to carry out in one reacting volume, in any sequence, without depressurization and contact to environment almost all chemical engineering processes, namely: dissolution, synthesis, crystallization, filtering, washing, distillation, vibrating fluidized-bed conductive drying, extraction, crushing etc. [3- 9]. Basic differences of the multifunctional chemical reactor consist in a way of leading of energy for stirring - in the form of the adjustable low-frequency harmonic vibrations brought to the working volume from the outside. There are no mixing devices and seals in the chemical reactor. The working chamber is autonomic, easily removable, has an elementary geometrical form, without stagnant and difficultly washed out zones. Drying is carried out by conductive way in fluidized-bed. Vacuum drying through filtering knot excludes carry-over of a solid phase. The gas heat-carrier is not applied. The reactor design excludes even potential sources of an impurity and pollution of an obtained product, provides hydrodynamic similarity of course of technological processes and their scaling for volumes of the working chamber to 160 litres.

At necessity, the internal surface of the working chamber can be made absolutely corrosion-resistant - from fluorine plastic. Analogues of the development are absent. The development is patented in the Russian Federation.

Testing the pilot variant of the vibrating multifunctional chemical reactor in volume of 40 litres were carried our under production conditions the chemical-pharmaceutical enterprise at separate stages of chemical synthesis of substances of medical products. It has been shown that application of low-frequency vibrations allows to intensify considerably all without an exception listed above technological processes. Especially filtering and drying processes – as it is known, it is "bottlenecks" of any work cycle. Influence of each of vibration parameters (frequency, amplitude, acceleration of vibrations) on character of processes has been established.

On the basis of vibrating multifunctional chemical reactors the automated flexible system can be created, that allows the following: - the control and maintenance of demanded technological and time parameters at each stage of realized technological processes with a conclusion of the information to the display and the printer; - works in an automatic or dialogue mode; - tasks of an order and optimum sequence of actions of the operator at each stage of the process; - automatic blocking of not procedural actions of the operator. Transition to output of a new product on FCTS does not exceed 1 hour.

Almost all groups of products of small-scale chemistry can be an area of practical application of vibrating multifunctional chemical reactors: first of all, manufactures of the most difficult in technology hormonal, endocrine, anti-tumor, etc. substances of synthetic medical products, and also - chemicals and especially pure substances, - organic pigments and semi-products, - stabilizers, -fire-retardants, - toxic, especially dangerous and poison substances. The overall amounts of products of these groups exceeds 50 000 names, the majority of them are not made in Russia and are imported from abroad.

References

[1]. Chistovalov S.M., Chernov A.N. J. Chemical and Petroleum Engineering, **1996**, #3, P35
[2]. Chistovalov S.M. , Chernov A.N. J. Chemical Industry **1997**, #8, p.563-567
[3]. Chistovalov S.M., Chernov A.N. Patent RF # 2042373, **1995**
[4]. Chistovalov S.M., Chernov A.N. Patent RF# 2089258, **1997**
[5]. Chistovalov S.M., Chernov A.N. Patent RF # 2293594, **2007**
[6]. Chistovalov S.M. Patent RF # 2290245, **2006**
[7]. Chistovalov S.M. Patent RF # 2287354, **2006**
[8]. Chistovalov S.M Patent RF # 2340382, **2008**
[9]. Chistovalov S.M. Patent RF# 2367495, **2009**

PP-II-13

THE ANALYSIS OF INFLUENCE OF TECHNOLOGY FACTORS ON MMD NEODYMIUM RUBBER

Diakonov G.S., **Aminova G.A.**, **Manujko G.V.**, **Bashkirov D.V.**, **Ignashina T.V.**

Kazan state technological university,
K. Marx str., 68, Kazan, 420015, Russia, a_guzel@mail.ru

One of major factors influencing properties of obtained polymer is the temperature in cascade reactors. Including at multiple feeds on cascade reactors the basic influence on molecular mass distribution is rendered by temperature changing as a result of the additive in the reactor. The temperature belongs to the number of factors most strongly influencing the course of chemical-technological processes, and mostly on the course of chemical reactions. Therefore when analyzing and modeling the equipment, in particular chemical reactors, a careful account of thermal factors is necessary: i.e. emission, absorption and transfer of heat. Generally, it is possible to specify at least, two important results exothermic. First, the incomplete heat-removal in the course of an exothermic reactions results in thermal auto acceleration and can become the reason of the reaction instability. Second, the temperature change influences such basic properties the polymer as average molecular weight and molecular-mass distribution (MMD).

The mathematical model of rubber SKDN synthesis in the cascade of the continuous reactors for various schemes of input mixture, consisting of kinetic and power modules is developed. The milestone of account of reactors consists in a solution of the stationary equations at the given condition of a base mixture, at required performances of finished products. On the basis of offered mathematical models influence of conditions of polymerization on change MMD of products of polymerization is theoretically investigated. With increase in the flow rate of secondary flow mixture average molecular-mass characteristics decrease, and this tendency amplifies with growth of temperature of secondary flow. Proceeding from the carried out researches it is possible to draw a conclusion that the basic influence on molecular-mass characteristics is rendered by temperature changing as a result of the additive in second reactor.

The analysis of dependences of molecular-mass and physical-mechanical characteristics of finished products from conditions of performance process allows to choose the most suitable rational conditions in each case according. Moreover, similar schemes of multiple feeds allow to obtain rubber on neodymium catalyst with properties new for this process.

NOVEL MICROREACTOR FOR THE WATER-GAS SHIFT REACTION ON THE BASE OF Mo_2C CATALYST

Dubrovskiy A.R.[1,2], **<u>Kuznetsov S.A.</u>**[1], **Rebrov E.V.**[2], **Schouten J.C.**[2]

[1]*Tananaev Institute of Chemistry, Kola Science Centre RAS, 26 Akademgorodok, 184209 Apatity, Russia, E-mail: kuznet@chemy.kolasc.net.ru*
[2]*Departmant of Chemical Engineering and Chemistry, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands, E-mail: e.rebrov@tue.nl*

A water-gas shift catalyst for an automotive fuel processor should demonstrate sufficient activity in the temperature window between the reformer and PrOx reactors, have at least 5000 h stability, be non-pyrophoric, and provide a fast start-up. A commercial $Cu/ZnO/Al_2O_3$ catalyst has been used between the operating temperatures of 453 and 523 K. The temperature stability is poor above 523 K and it is pyrophoric if exposed to air. The catalytic coatings are usually deposited by wash-coating on the inner walls of the microchannels. Recently developed Mo_2C catalysts showed a higher activity in the WGS reaction as compared with the commercial $Cu/ZnO/Al_2O_3$ catalyst [1]. They have also high stability against oxidation under reaction conditions, and do not catalyze the methanation reaction at elevated temperatures.

A novel microstructured reactor/heat exchanger (MRHE) containing eight sections with each a cross-section of 10 mm x 10 mm and a length of 100 mm has been designed and constructed based on the kinetic model [2]. Each section of the reactor compartment contains flat, perforated Mo plates and Mo wires with a diameter of 250 μm and a length of 100 mm coated with a porous Mo_2C layer. In the MRHE, the reactant mixture enters at 673 K and follows the optimal temperature profile which allows to minimize the reactor volume as compared with isothermal operation. The anode fuel cell gas preheated to 533 K is used as a coolant. Two coolant side streams are required to approach the optimal temperature profile in a counter-current MRHE. The start-up time required to heat the MRHE up to the operational temperature does not exceed 2 minutes.

References

[1]. A.R. Dubrovskiy, S.A. Kuznetsov, E.V. Rebrov, J.C. Schouten, Doklady Chem., **(2008)**, 421, 186.
[2]. E.V. Rebrov, S.A. Kuznetsov, M.H.J.M. de Croon, J.C. Schouten, Catal. Today, **(2007),** 125, 88.

THE WAYS OF RISE THE PRODUCTIVITY OF ETHYLENE OXYCHLORINATION REACTORS

Flid M.

Scientific Research Engineering Centre “Syntez”, Moscow, Russia.
E-mail: mflid@yandex.ru

The main trend in the activities of leading producers of vinyl chloride is the intensification of existing manufactures that would increase the product manufacturing in 1,5-2 times by increasing the unit capacity of reactor units.

The main problem of the rise in the productivity of industrial reactors of ethylene oxidative chlorination (oxychlorination) is the lack of balance between the kinetic productivity of catalysts and heat removal. A high value of heat of ethylene oxychlorination (238 kJ/mol) necessitates the use of an array of fixed-bed catalytic reactors where each reactor contains catalysts with different compositions and activities. The process temperature is 280–300°C. The processes of ethylene oxychlorination in the fluidized bed of the catalyst (usually the systems $CuCl_2/\text{-}\gamma\ Al_2O_3$) require lower (210–230°C) temperatures.

Heat is removed by evaporating 10–15% of the boiling water in the cooling coils immersed in the catalyst bed.

The productivity of low-temperature catalysts that provide at least 99% conversion of HCl is 1100–1400 g/(l Cat h). The real amount of the catalyst charged into the industrial reactor is 3–3.5 times greater than the minimum amount. This is usually associated with the impossibility of placing cooling devices in the limited volume of the catalyst bed. The intensification of heat removal and an increase in the reactor productivity is possible only if the temperature gradient Δt between the coolant and the catalyst bed is increased.

When low temperature catalysts are used, Δt is 40–45°C. An increase in the temperature of the process to 235–240°C leads to a decrease in the selectivity of the process and formation of chloroorganic by-products and the products of deep oxidation (CO and CO_2).

Paradoxically, the productivity of industrial fluidized-bed catalytic reactors can be increased by using catalysts with a lower activity. A decrease in the activity of alumina-based catalysts is usually achieved by adding alkali or alkali earth metal (Me) chlorides, most frequently K and Mg. These additives in an atomic ratio Me/Cu of 1–2.5 lead to a decreasing rate constant of oxychlorination at 220°C by a factor of 3–5. The complete conversion of hydrogen chloride can be achieved, in this case, by an increase in temperature to 245–255°C. The process selectivity remains 98–98.5% because the rate of ethylene oxidation or dichloroethane oxidation to form CO*x* usually changes in a like manner together with a change in the rate of the main reaction of oxychlorination.

When the oxychlorination of ethylene is carried out in the fluidized bed of the catalyst, one of the major conditions is to maintain high quality fluidization. Specifically, conditions favorable for the agglomeration of catalyst particles should be excluded.

An increase in the productivity of the reactor assumes an increase in the flow rates of initial reactants, which, in turn, affects the hydrodynamics of the fluidized bed. The flow rate of gases is limited by the minimum fluidization rate. For number of quantity of industrial catalysts of the fluidized bed, 20–100 μm particles and a bulk density of 1.00–1.10 g/cm^3 are typical. The minimum fluidization velocity is 3.5–5.0 mm/s depending on the nature of the fluidizing agent.

Proceeding from the threshold value of the fluidization number which is 77.7 for the laminar flow, the maximum value of the working gas flow rate in the industrial reactor is 0.27–0.39 m/s.

Industrial processes in which concentrated oxygen is used as an oxidant are more flexible compared to the process in which air is used, because an increase in the consumption of initial reactants is possible with a simultaneous decrease in the flow rate of the recycled gas, which is both a fluidizing agent and a diluent that provides explosion safe conditions of the process. Also the air based process can be intensified by enriching the air with oxygen to a concentration of 23–24%.

One of the conditions for an increase in the productivity is the use of catalysts with a higher value of the equivalent diameter of particles. So, an increase in the effective diameter of particles from 50 to 100 μm leads to an increase in the minimum fluidization velocity from 3.5 to 13.0 mm/s. In this case, the working linear velocity of the gas flow can be increased up to 0.7–0.8 m/s with rise of the productivity.

If we consider a reactor and a catalyst as a mutually related system, the ways for increasing the productivity can be associated only with technological parameters of the process (flow rates of initial reactants and their concentrations, temperature, pressure and others).

SIMULATION OF HEAVY PARAFFINS DEHYDROGENATION REACTOR

Frantsina E.V., **Afanasjeva Y.I., Maksimova E.S.,**
Romanovskiy R.V., Ivanchina E.D.

Tomsk Polytechnic University, 634050 Tomsk Lenina sq., 30, evf86@sibmail.com

Simulator methods allow to execute a quantitative estimation of technological characteristics of manufacture and to raise its efficiency [1].

The presumable transformation scheme of the process was designed on the basis of the dehydrogenation mechanism. Electron molecule structures and reaction thermodynamic characteristics (ΔG_r, ΔH_r, ΔS_r) were estimated for conditions 753 K and 0,2 MPa using the quantum-chemistry calculation methods (Gaussian program package containing PM3 procedure of NDDO method) [2].

Thus the results show that aromatization reaction appears to be the most thermodynamically probable ($\Delta G^0_r \approx -300$ kilojoule/mol). Paraffins and olefines isomerization reactions do not occur in the present process. Also the reactions of dienes formation with cumulative double bonds are not thermodynamically allowed ($\Delta G^0_r \approx -5$ kiloJoule/mole). The presence of isomeric paraffins in the product is determined by iso-paraffins dehydrogenation processes which are present in raw materials. All other possible reactions are thermodynamically probable and have approximately the same value of isobaric-isothermal potential ($\Delta G^0_r \approx -70$ kilojoule/mol). In the process the dienes with conjugate and secured double bonds are obtained, whereas formation of dienes with cumulative double bonds is not thermodynamically allowed under these conditions. Cracking ($\Delta G^0_r \approx -140$ kilojoule/mol) and coke formation ($\Delta G^0_r \approx -510$ kilojoule/mol) are the main by-reactions.

On the basis of these results the formalized scheme of higher alkanes C_9-C_{14} dehydrogenation process was designed. Formalization layer of transformation compounds mechanism assumes the aggregation of pseudo components into groups according to reactionary ability that is evaluated according to isobaric-isothermal potential ΔG_r. Thus 11 groups of pseudo components were formed that participate in 22 types of chemical reactions.

Kinetic model was developed according to the law of active mass and formalized transformation scheme. Effective rate constants are combination of all intermediate stages. Kinetic parameters (preexponential factors k_0 and activation energies E_a) for all chemical reactions were calculated by decision of a inverse kinetic problem, that was realized in integrated environmental Delphi 7. The data used as input in the calculation are physic-chemical properties of hydrocarbons, components composition and product mixture, technological conditions that are obtained from generated in Microsoft® Office Access 2007 data basis.

Diffusion Pe_D=2375-1663 and thermal Pe_T=2494 criterions Péclet estimation confirms the possibility usage of ideal spilling reactor for mathematical description of hydrodynamic regime.

For model verification the calculated characteristics of the output flow were compared to similar experimental values from industrial reactor. The average deviation of input concentration did not exceed 4 % that confirms high accuracy of process model kinetic parameters.

Method for increasing of efficiency of the linear alkyl benzenes manufacture was offered with usage developed mathematical model of dehydrogenation reactor. Influence of water such as inert addition in desired reaction and active continent in reaction of steam-water conversion was investigated. It is shown that water concentration was varied within the limits of 2 to 3,5 liter/hour that led to decrease in the coke concentration up to 2,9 mass %. That dynamics of water delivery allows extending the life cycle of catalyst 5 %.

References

[1]. Kravtsov A.V., Ivanchina E.D., Ivashkina E.N. Yuriev E.M. Improving the process of higher paraffin dehydrogenation on the basis on nonstationary kinetic model // Abstracts of «XVIII International conference on chemical reaction CHEMREACTOR-18». – Novosibirsk: Punlishing house Boreskov Institute of Catalysis SB RAS, 2008. – P. 325-326.

[2]. Hyrsan S.L. Quantum mechanics and chemistry. – Ufa: PE Rayanov, 2005. – 164 p.

PP-II-17

OPTIMISED METHOD TO DEPOSIT CATALITIC MATERIALS ON STRUCTURED SURFACES

González O., Unzurrunzaga A., Pérez S., Belsué M.

INASMET-TECNALIA, Energy Unit, Bioenergy Department, Mikeletegi Pasealekua, 2
Parque Tecnológico - Teknologi Parkea, E-20009 Donostia - San Sebastián (Spain),
orlando.gonzalez@inasmet.es

Abstract

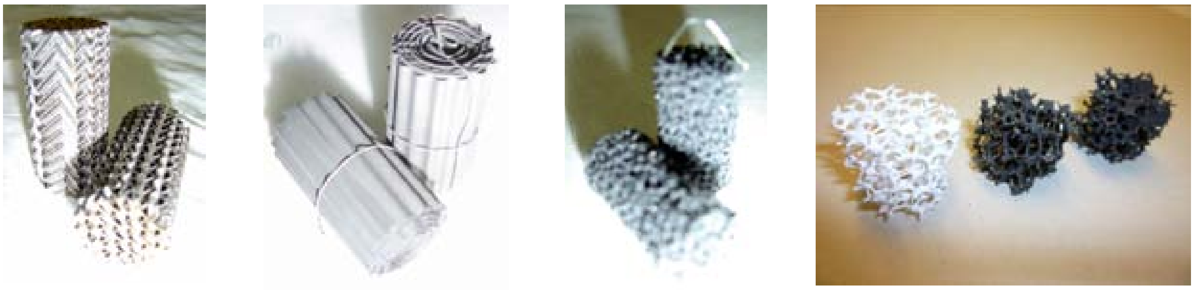
Process Intensification (PI), which is defined as "any chemical engineering development that leads to a substantially smaller, cleaner, safer and more energy efficient technology", is likely to be the next revolution of the chemical industry. The need for more efficient processes, including further flexible engineering designs and, at the same time, increasing the safety and environmental impact of these processes, is putting pressure on the industry to do novel R&D in this field. The field of **structured catalysts is included in the PI concept**. These devices are comprised by rigid 3D structures made of metal or ceramic materials, with pores or channels exhibit a large side surface on which a catalytic material thin layer can be deposited and through which a fluid can circulate. These systems are suitable for replacing conventional packed beds of catalysts pellets in multitubolare externally cooled reactors with substantially enhanced heat exchange properties. Additionally, they offer great advantages related to low pressure drop and high flow rates commonly used in technologies or processes related to environmental (NOx, SOx and VOC´s abatement) and renewable energy issues (hydrocarbon reforming processes to produce hydrogen or syngas from several sources, such as: carbon, natural gas, biomass, liquid hydrocarbons, etc.). *A catalytic coating method based on a liquid phase has been optimised in this work* in order to prepare structured catalysts. Our group has developed a know-how on washcoating deposition techniques of catalyst layer of different composition (e.g. carriers based on mesoporous SiO_2 and Ni-Co catalysts supported on them) onto supports with different geometries (structured packing, monoliths, and SiC and Al_2O_3 foams).

Experimental: Four types of structured devices with cylindrical dimensions (16 mm OD x 25 mm L) were used in this study as structured supports: home made parallel channel metallic monoliths using FeCrAlloy® sheets; KATAPAK®, commercial structured metallic packings; home made Al_2O_3 foams and ULTRAMET® SiC foams (see Fig.1). Metal structure supports were pretreated by thermal oxidation using air at 900°C/22h with the aim of generating a very rough surface of α–Al_2O_3

whiskers, which assure an appropriate morphology to anchor the catalytic coating on it. Catalysts of Ni-Co/SBA-15 and Ni-Co/SBA-15K with 15 wt.% Ni and 10 wt.% Co were prepared by the incipient wetness technique [1], simultaneously adding suitable amounts of an aqueous solution of Ni and Co hexahydrated nitrates (99.9%) to the SBA-15 mesoporous silica (fresh and previously modified with K) [2]. By using of a centrifugal ball mill, grinding parameters were optimized in order to reach an appropriated particle size for the preparation of stable slurries. The catalyst slurries were prepared by optimization of some variables, such as: catalyst particle size (D_p), solids content, and binder content (Nyacol® and Disperal® suspensions) [3]. Viscosity and pH of the slurries were measured. Coating deposition step was optimized by controlling others experimental variables, such as: immersion time, dipping and withdrawing speed, centrifugation velocity to eliminate the excess of slurry, dry and calcination temperatures of the coated samples and the use of primer. The quality of catalyst coatings was evaluated in terms of loading, homogeneity and adhesion force. The adherence of coating was evaluated in terms of weight loss after exposure to ultrasonic treatment.

Details about the preparation method of these kind of catalytic devices are showed therein. Also are included relevant reactivity results obtained by using of structured catalysts in the total oxidation of acetone, catalytic autothermal reforming (ATR) of iso-octane and thermo-catalytic decomposition of methane (DTC).

Fig. 1. Devices used for the preparation of structures catalysts.



KATAPAK-M® packing

Fecralloy® monoliths

ULTRAMET® SiC Foams

Non-washcoated and washcoated Al_2O_3 Foams

References

[1]. G. Leofanti, M. Padovan, G.Tozzola, B. Venturelli*, Catal. Today* 41 (1998) 207.
[2]. K. Flodström, V. Alfredsson, *Microp. Mesop. Mater.* 59(2003) 167.
[3]. S. Zhao, J. Zhang, D. Weng, X. Wu, *Surf. Coat. Technol.* 167 (2003) 97.

PP-II-18

REACTOR MODELING AND SIMULATION OF MOVING-BED CATALYTIC REFORMING PROCESS

Gyngazova M.S., Kravtsov A.V., Ivanchina E.D., Korolenko M.V.

Tomsk Polytechnic University, Tomsk, Russia, E-mail: gyngazova@mail.ru

Catalytic reforming is one of the most important processes for high octane gasoline manufacture and aromatic hydrocarbons production. A number of research papers is devoted to mathematical modeling of this process [1-9]. Presence of many components as reactants and intermediate products in the reaction mixture makes a problem of modeling difficult. To decrease the complications reactants in the mixture are classified in certain and limited groups called pseudo components. The number of selected pseudo components in the mixture is a determinating factor for model design. Obviously, the more the number of specified pseudo components are the higher the accuracy of the model will be, but at the same time this leads to more complicated mathematical formulation. There is a need to develop a universal mathematical model that could balance this contradiction and that could be used for different raw material compositions.

Previously [10] we analysed the set of possible reactions, proposed kinetic model for catalytic reforming process, calculated thermodynamic and kinetic parameters, investigated catalyst layer hydrodynamics.

The model of moving-bed catalytic reforming reactor, presented by a system of equations of material balance for components and the equation of heat balance is the following:

$$\begin{cases} G\cdot\frac{\partial C_i}{\partial z}=-u\cdot\frac{\partial C_i}{\partial r}-\varphi\cdot\frac{\partial C_i}{\partial l}+\int\limits_0^l W(l)a(l)dl \\ \rho^m\cdot C_p^m\cdot G\cdot\frac{\partial T}{\partial z}=-u\cdot\rho^m\cdot C_p^m\cdot\frac{\partial T}{\partial r}-\varphi\cdot\rho^{cat}\cdot C_p^{cat}\cdot\frac{\partial T}{\partial l}+\sum Q_j\cdot\int\limits_0^l W_j(l)a(l)dl \end{cases}$$

at z=0 $C_i=0$; at l=0 $C_i=C_0$ (at the reactor entrance); at r=0 $C_i=C_0$;

z=0 T=0; at r=0 $T=T_{en}$; at l=0 $T=T_{en}$

where z – volume of raw material processed, m^3; G – raw material flow rate, m^3/h; C_i – concentration of i-th component, mol/m^3; u – flow rate, m/h; r – radius of catalyst layer, m; l – catalyst layer length in the reactor, m; φ - catalyst flow rate, m/h; W – integral reactions rates for component i, $mol/(m^3\cdot h)$; a – catalyst activity;

c^m, c^{cat} – density of mixture and catalyst, kg/m^3; C_p^m, C_p^{cat} - heat capacity of mixture and catalyst, J/(kg·K); Q_j – j-th reaction heat, J/mol; T – temperature, K; W_j – j-th reaction rate, mol/(m^3·h).

In moving-bed reactors catalyst activity changes through the radius and height of catalyst layer and with time. The coke concentration can be calculated according to the kinetics of coke formation. The catalyst activity will decrease with the coke concentration increase and will depend from the catalyst circulating factor (h_{cir}) the following way: $a = A_0 \cdot e^{-\alpha \cdot C_{coke}/h_{cir}}$

where A_0 – linear component determining the number of catalyst active centres; α – coefficient of catalyst poisoning - nonlinear component that determines different extent of angle and edge atoms deactivation due to coking. Calculations show that $3 \le \alpha \le 5.9$ - for reactions on metal sites of catalyst; $0.3 \le \alpha \le 0.52$ - for reactions on acid sites of catalyst.

Catalyst circulating factor can be calculated as: $h_{cir} = \dfrac{u \cdot \rho^m}{\varphi \cdot \rho^{cat}}$

In this work we have presented a mathematical model for a moving-bed catalytic reforming reactor taking into account activity and circulating factor of the catalyst.

References

[1]. Smith R.B. Kinetic analysis of naphtha reforming with platinum catalyst // Chem. Eng. Prog., 1959, №55(6), p. 76-80.

[2]. Krane H.G. Reactions in Catalytic Reforming Naphtha // Proceeding of the 5th World Petroleum Congress , 1959, p. 39- 51.

[3]. Zhorov Y.M. Mathematical Description of Platforming for Optimization of a Process (I) // Kinetika i Kataliz, 1965, №6(6), p. 1092 – 1098.

[4]. Henningsen J. Catalytic Reforming // Chem. Eng., 1970, №15, p. 1073 -1087.

[5]. Kmak W.S. A Kinetic Simulation Model of the Power Forming Process ;AIChE Meeting, Houston, TX, 1972.

[6]. Marin G.B. Froment G.F. The Development and Use of Rate Equations for Catalytic Refinery Processes // EFCE Publ. Ser., 1983, Vol 2. , №27, p. 117.

[7]. Froment G.F. Modelling of Catalytic Reforming Unit // Chem.Eng.Sci., 1987, №42, p. 1073 – 1087.

[8]. Unmesh Taskar & James B.Riggs Modelling & Optimization of Semi Regenerative Catalytic Naphtha Reformer // AIChE J., 1997, №43 (3), p. 740 – 753.

[9]. Sharikov Yu.V., Petrov P.A. Universal model for catalytic reforming // Chemical and Petroleum Engineering, 2007, vol. 43, p. 580-584.

[10]. Gyngazova M.S., Kravtsov A.V., Ivanchina E.D., Abramin A.L. Computer modeling of catalytic reforming process in moving-bed reactor with continuous catalyst regeneration // Abstracts XVIII International Conference on Chemical Reactors CHEMREACTOR-18, Malta, 2008, p. 127–128.

PP-II-19

NEW BASIC SHAPE OF CATALYSTS IN NATURAL GAS REFORMING REACTOR

Hartmann V.L.[1], **Obysov A.V.**[1], **Dulnev A.V.**[1], **Afanas'ev S.V.**[2]

[1]*LLC "NIAP-KATALIZATOR", vhart@yandex.com*
[2]*JSC "Togliattyazot"*

The common present-day tendency when revamping ammonia or methanol plants is to use the existing equipment to the utmost extent. Nowadays, the bottleneck stage of such a plant is the tube furnace. The ordinary way to eliminate it is to use tubes with a greater inner diameter and an increased amount of the same catalyst. But, with a plant upgraded from 1360 to, say, 1800 mtons per day, it is quite expensive concerning both tubes themselves and the catalyst volume needed. Besides, the problem arises of heat transfer through walls of wider tubes.

As it was mentioned in [1], the performance of a catalyst bed in hydrocarbons reforming is mainly proportional to catalyst bed surface area, m^2/m^3. To verify this fact, some samples of both out- and up-to-date nickel-alumina natural gas (NG) reforming catalysts with more than 6% of NiO were tested using the gradient-free unit PKM-1 (Boreskov Institute of Catalysis). The discrepancy in activation energy and prefactor values lies mainly within the limits of experimental scatter.

Thus a more competent solution is to increase catalyst specific bed surface area. On the other hand, according to common approach [2], pressure drop across a granular bed is expressed as:

$$\Delta P/L = 0.5 f_e \rho w^2 a \varepsilon^{-3} ,$$

$\Delta P/L$ – pressure drop per unit bed length, Pa/m; f_e – drag (or friction) factor; ρ – gas density, kg/m^3; w – superficial linear gas flow velocity (per full bed cross-section), m/s; a – specific bed surface area, m^2/m^3; ε – bed porosity, m^3/m^3.

Thus, such a way can lead to a high pressure drop across the bed, which, in its turn, leads to the gas compressor enormous energy consumption or even issues.

It is commonly accepted that f_e is a universal function of the Re number, its variation for granules of different types being limited to 30% [2]. So, the only way to avoid an increase in the pressure drop is to enlarge bed porosity. On this way NG reforming catalyst granules have evolved from simple cylinders (Cylinder in the Table 1) to multiperforated ones with rounded faces and even grooves. Unfortunately, granule internal porosity increase is limited by mechanical strength decrease. So, the potential of the cylinder based shapes was exhausted at the very beginning of the new millennium. The only way out was to change the basic shape to the other one with greater external porosity.

The idea is as follows. The minimal porosity of cylinders dense packing is 9%. The same figure for spheres is 26%. One can expect that the external porosity of real (disordered) bed of spheres is greater than that of cylinders.

Fig. 1. New spherical support.

It should be mentioned that the attachment to cylindrical shape is due, mainly, to the fact that the raw support granules are tabletted, and nobody succeeded to tablet even the cylinder with strongly convex faces (Cylinder2 in the Tables).

Cylinders with such faces or spheres can be made by a ceramics technology.

The appearance of perforated porous corundum spheres (Sphere1 and Sphere2 in the Tables) hereby produced are shown on fig.1.

Table 1. Characteristics of some NG reforming catalysts.

Basic characteristics	Cylinder	Ring	Cylinder2	Sphere1	Sphere2
Diameter (mm)	15	15	16	16	10
Height (mm)	15	12	14	-	-
Holes, number×diameter (mm)	-	1×6	7×3	7×3	7×2
a (m^2/m^3)	180	330	430	450	730
ε, (m^3/m^3)	0.35	0.51	0.52	0.62	0.68

The tube (inner diameter 89 mm) furnace of a Kellogg ammonia plant was recently loaded with the nickel-alumina spherical catalyst (Sphere1 type). Table 2 shows catalyst performance data compared with those of the predecessor (Cylinder2 type) in the same furnace at the start of its run 7 years ago.

Table 2. Performance data of the catalysts in the tube furnace.

Catalyst type	NG input flow (kmol/hr)	Inlet pressure (bar gauge)	ΔP (bar)	T_{out} (°C)	Steam to NG ratio	$[CH_4]_{out}$ (vol %)
Sphere1	1.8×10^3	30	1.4	796	3.6	9.5
Cylinder2	1.8×10^3	28	2.6	790	3.7	10.4

References:

[1]. Temkin M.I. *Advances in Catalysis*, **1979**, v.28, p.173.

[2]. Aerov M.E., Narinskiy D.A., Todes O.M. *Apparatuses with static granular bed* // Khimiya – Leningrad, **1979**.

PRODUCING OF THE SYNTHESIS-GAS AND FINE-POWDER SOOT IN THE MODIFIED REACTOR OF OXIDIZING PYROLYSIS BY THE ELECTROCHEMICAL WAY

Huseynova F.K.

National Academy of Sciences of Azerbaijan, Institute of Chemical Problems,
Farida_az@inbox.ru

The special reactor - ECCC (the electrochemical combustion chamber) and also the technique of acetylene producing in this device had been created and patented for the acetylene production by the incomplete oxidation of natural gas method with imposition of diffusive discharge on the reacting space /1/. This method is topical still present because of the target product output on this device reached14-15 % (for comparison: output C_2H_2 on used now industrial units are only 7-9 %).

The basic characteristics of this process in the reactor ECCC is modified pyrolysis of a mixture of natural gas and oxygen with oxidizer surplus factor $\alpha \leq 0.4$, pressure 0.98·105 Pa, with diffusive discharge imposition on reacting space at voltage between electrodes 400 - 800 V, and maximum of the reactions temperature changes between 1400-2800°K.

Process is complex multi-parameters one because there are participate from 10 to 14 reactions in its kinetics scheme; it is depend from the chosen version of parameters. For management of such complex process with 16 operating parameters, its mathematical model had been work up with considering all features of experiments implemented ECCC design. The model had been identified on the base of thermodynamic and kinetic calculations very precisely /2, 3/ and had allowed to make an explanation and clearance of instability of some modes chosen during experiments (a fire torch attenuation, products very much burning, the reactor breakdown, etc.) /4/.

After the mathematical model identification by means of spent experiments and verifying it is completely adequate to process, the theoretical optimization of the process was been made with the goal to study all opportunities of this device and process. During the optimization of process it has been describes theoretically the acetylene output can reach 25 % if the adequate heat resisting material for reactor made would be found. And the reached in experiments output 14.75 % is maximal for a used material /5/.

At the analysis consist of the real pyrogas (produced at experiments) and, in the further, data of the process theoretical optimization and calculating experiments for various process parameters had been noticed that except for acetylene which was an initial target product, other valuable products exist in the pyrogas structure that can become independent targets and products owing to its demand in a science and in the modern industry.

At first stage during experiments these products had been displeased since complicated the ECCC experiments course and operating conditions selection. Such products became a mixture of hydrogen and carbon monoxide gases (CO + H_2) named synthesis-gas and fine-powder soot C (which is condensed from gaseous carbon) which turns during combustion of raw materials.

By results of thermodynamic and kinetic calculations on mathematical model the greater share in pyrogas have molecular hydrogen H_2 and carbonic monoxide CO, atomic carbon C. One of these products is topical now as fine-powder soot is actual product in the industry for producing ebonite, rubbers, some plastic masses, etc. The mixture of others is known as a synthesis-gas is the best alternative fuel for motor transport and only difficulties in its production are a delay for applying.

The synthesis-gas is considered as alternative fuel as more relevant for using because of reduction of explosion hazard of pure hydrogen is offered. As share of CO is approximately in 3 times less than H_2 in the pyrogas it was offered to lead process optimization not on each component of this mix, and on synthesis-gas as a joint target product.

By results of calculating experiments the maximal synthesis-gas output is possible 60 volumetric % in structure of pyrogas in ECCC at various modes, but it is reached at greater value of the enclosed enthalpy, than for an optimum output of acetylene, I =11.3 mln. J/kg CH4. Modes in which only 45-55 vol.% are most achieved and stable.

Data of calculating experiments at which synthesis-gas output makes 30-35 vol. % have been obtained for $\alpha = 0.2$ and enclosed enthalpy I = 9,5 mln. J/kg CH4.

At kinetic process calculations energies of water and carbon condensations were not considered, though the caused by these processes anomalies were visible on temperature curves. It has been made because of the sharp necessity in them is absent for the adequate mathematical model determination, and because of authors unwillingness complicated full enough process model much also with added parameters.

Also the maximal soot output operating conditions parameters for laboratory ECCC achieved at specific enclosed enthalpy I = 15 mln. J/kg CH_4, thus the soot output revealed 3-5 vol.%. This percentage is reached at the temperature peak 2300-2400°K. It means there is fuller pyrogas hydrocarbons combustion and certainly the acetylene share is insignificant, but it is not allow possible to set criterion function for both products producing in one mode.

REFERENCES

[1]. Bayramov T.A., Karayev R.A., Shakhtakhtinsky T.N., etc. “ Acetylene producing technique and device for it implementing”, Patent № 1290702, USSR, 1986.

[2]. Huseynova F.K., Karayev R.A.Thermodynamic analysis of methane oxidation and pyrolysis prosess at high temperatures, Azerbaijan Chemical Journal, 1986, No.4, p. 16-23 (in Russian) .

[3]. Huseynova F.K., Karayev R.A. Kinetics of methane oxidation pyrolysis under Joule heating, Journal of Applied Chemistry, 1992, V.65, issue 6, p.1337-1341 (in Russian) .

[4]. Huseynova F.K., Karayev R.A., Bayramov T.A. Mathematical model of electrochemical combustion chamber, dep. Institute of scientific and technical information of USSR, 31.10.1991, No. 4173-B91 (in Russian).

[5]. Huseynova F.K., Karayev R.A., Romanyuk I.M. Modeling of reactors of oxidation pyrolysis of methane, Theoretical Foundations of Chemical Engineering (TOXT), 1995, V.29 (1), p. 29-33.

PP-II-21

MODELLING OF CATALYTIC HYDROLYSIS OF METHYL FORMATE

Jogunola O.[a,*], Wärnå J.[a], Mikkola J.[a,b], Salmi T.[a]

[a]*Laboratory of Industrial Chemistry and Reaction Engineering,*
Process Chemistry Centre, Åbo Akademi University, Biskopsgatan 8,
FI-20500 Turku/ Åbo, Finland. Fax: +35822154479.
[b]*Umeå University, Technical Chemistry, Chemical-Biological Centre, Department of Chemistry, SE-90187 Umeå Sweden*
**Corresponding author: jolatund@abo.fi, ph: +35822154431*

Hydrolysis of ester is among the most important reactions in the fine chemical industry. The reaction is slow at neutral pH but can be accelerated under acidic conditions. HCl [1] has been reported to catalyze the hydrolysis of ester such as alkyl formate successfully. However, only very few researchers have studied the hydrolysis of alkyl formate (ethyl formate) using acidic ion exchange resins [2]. Moreover, there has not been a single report on the hydrolysis of methyl formate with the resins.

The liquid-phase hydrolysis kinetics of the methyl formate was determined in a laboratory-scale batch reactor using Amberlite IR 120 resin (d_p = 0.3 – 1.2 mm) as a catalyst. The reaction rate is described as:

$$r_i = k + k'C_C\left(C_A C_B - \frac{C_C C_D}{K_C}\right) \tag{1}$$

where k = uncatalyzed rate constant, k' = rate constant of the autocatalytic process, K_C = concentration-based equilibrium constant, C = concentration.

During the course of study of the hydrolysis process, internal diffusion affected the kinetics. A mathematical model, which incorporates the particle size distribution of the solid catalyst, was developed to reveal the kinetics and internal mass transfer effects of the porous particles. The model equations were solved with the software Modest [3]. The mass balance for the bulk phase is

$$\frac{dC_i}{dt} = a_p \sum_j y_j N_{ij} x_j^2 + r_i \tag{2}$$

where a_p = interfacial area-to-volume, y_j = frequency function for particle size distribution, x = dimensionless coordinate and N = flux. The mass balance for the catalyst particles is

$$\frac{dC_i}{dt} = r_i + \frac{r_i \rho_p}{\varepsilon_P} + \frac{D_{ei}}{\varepsilon_P R_j^2}\left(\frac{d^2 C_i}{dX^2} + \frac{a-1}{X}\frac{dC_i}{dX}\right) \tag{3}$$

with the boundary conditions $C_{i(X=1)} = C_i$ at the particle surface and $\left(\frac{dC_i}{dt}\right)_{X=0} = 0$

A numerical algorithm and software were developed to estimate the parameters and predict the concentrations in the bulk phase and inside the catalyst particles. The model was able to predict the experimental data and some of the fits of the model for some experiments is given in Fig. 1.

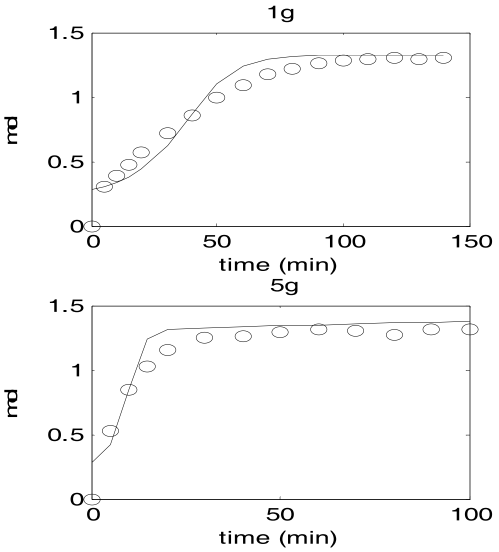


Fig. 1. Fit of the model to the experimental data for methyl formate at 60 °C and different catalyst loadings.

The concentration profile (mol/dm^3) of methyl formate inside the catalyst particle at 60 °C for different particle sizes (particle diameter in mm) at the beginning of the reaction is shown in Fig. 2. As revealed by the figure, diffusion resistance plays a major role in the process since most catalyst particles had the diameter range of 0.4 – 0.9 mm.

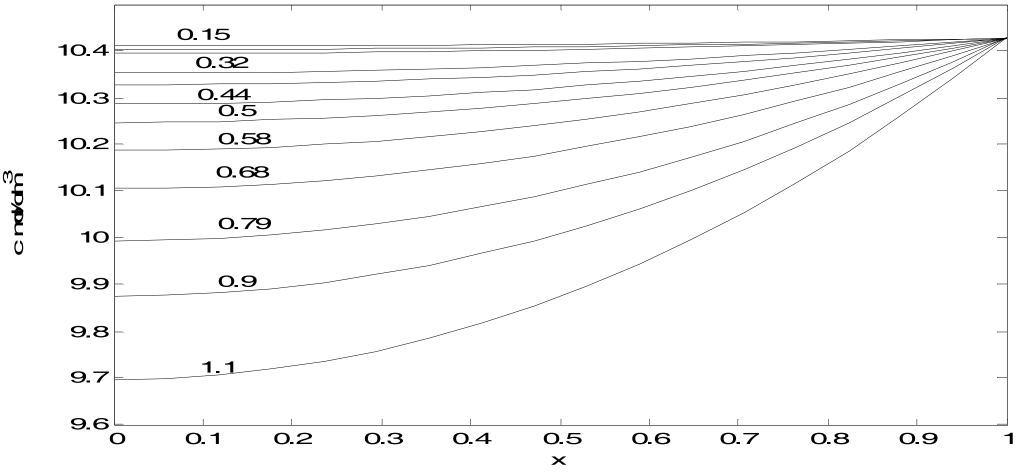


Fig. 2. Concentration profile of methyl formate inside the resin particle

References

[1]. Bell, R.P., Dowding, A.L., Noble, J.A., 1955. J. Am. Soc. 9, 3106-3110.

[2]. Metwally, M.S., Abel Razik, A., El Hadi M.F., and El-wardany, M.A., 1993, React. Kinet. Catal. Lett. Vol. 49(1),151-159.

[3]. H. Haario, 2007, ModEst 6- A User's Guide, ProfMath, Helsinki.

PARAMETERS OF MASS AND HEAT TRANSFER IN FIXED-BED CATALYTIC REACTORS: ON THE QUESTION OF ITS THEORETICAL PREDICTIONS

Kuz'min A.E.

Topchiev Institute of Petrochemical Synthesis RAS, kuzmin@ips.ac.ru

Let is consider a mathematical model of common catalytic reactor element (cylindric tube) with fixed bed of catalyst granules and, in general, more than one fluid flow (trickle-bed as common example). For closure of mass, momentum, heat energy balance PDE (or ODE in simplified models) system one must know a functional set of parameters - apparent reaction rate constants, coefficients of intraphase (effective diffusion, heat conduction etc.) and interphase (for flow/catalyst and flow/wall boundaries among them) transfer. For such a parameters one can apply dimensional analysis and obtain an equation like

$$Nm_r = \sum_i C_i Nm_{d1}^{\ n_{1i}} Nm_{d2}^{\ n_{2i}} \ldots \qquad (1)$$

where theory can define clearly only a "basis" of determining dimensionless numbers Nm_{d1}, Nm_{d2} etc.; for value definition of C_i and n_i one, as it is thought to be, must carry on a set of experiments at various conditions. As a rule, it deliver a huge, sometimes inconsistent data array that often can not be satisfactory described by only one correlation like (1) with one set of C_i, n_i etc. for overall conditions range. Such a procedure must be fulfilled for any of required numbers Nm_r (where a corresponding coefficient of a balance equation is included); a huge body of various papers is dedicated and was dedicated to these problems through decades. Is it possible to overcome tradition and to develop an alternative way for full determination of equations like (1) (or more complex) with a minimum set of experiments?

One can assume that a complex process taking place in a reactor (or in any other apparatus of chemical engineering) represents a hierarchical three-level structure: the first level – one of atomic-molecular-scale motions, the third – one of reactor-scale motions (level of balance ODE), and the second one represents a motions at any intermediate scales (turbulent vortices, film flows, bubble destruction/coalescence, local by-passes and dead zones etc.). Then, one can imagine an extremely idealized situation where a second-level motions does not exist, i.e. a reactor model coefficients are determined only by molecular-scale motions at any external conditions; that can be called “a model of ideal order”. Next, if all second-level (chaotic or self-organisational) phenomena have “turned on” then a complex process became realistic and values of its model parameters change. Hence, we propose the hypothesis: because all changes of a given system is determined *by the same imaginative transition* from “ideal order” to real situation, then all model coefficients change *simultaneously*. It can be described by ratios of corresponding dimensionless numbers like

$$\frac{Nm_{r1}(Nm_{d1},Nm_{d2},...)}{Nm_{r1-or}(Nm_{d1},Nm_{d2},...)}=\frac{Nm_{r2}(Nm_{d1},Nm_{d2},...)}{Nm_{r2-or}(Nm_{d1},Nm_{d2},...)}=\frac{Nm_{r3}(Nm_{d1},Nm_{d2},...)}{Nm_{r3-or}(Nm_{d1},Nm_{d2},...)}=... \quad (2)$$

where a numerators consist of Nm_r values for a real process, while a denominators do ones for “ideal order” situation. Thus, if we obtain an empirical correlation (the most correct, for a maximal range of conditions) for only one of PDE coefficients (a reference coefficient) and develop an “ideal order” equations for all ones (those are a theoretical, and, for several cases, well-known equations), we can predict real values of all other model coefficients than reference one.

Opportunities of this approach has investigated for effective diffusion, heat conduction, some interphase heat and mass transfer coefficients in fixed-bed reactor models. The results are questionable: an exact quantitative agreement between various relations of (2) type has not observed, and one can discuss about strictness of “ideal order” equations has tested. However, it seems premature to reject validity of hypothesis (2) as a matter of principle, and the results look encouraging enough for further research of the considered hypothesis (for example, for trickle-bed reactor model where more coefficients of PDE than for ordinary fixed-bed reactor are necessary, and an empirical correlations for it are investigated much lesser).

PP-II-23

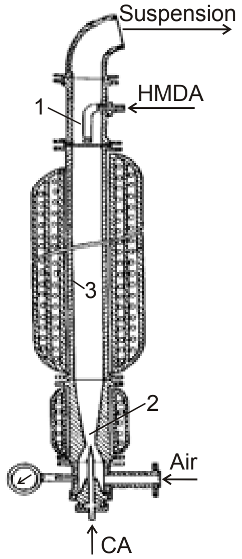
REAKTOR-FIBRIDATOR

Lagusseva E.I., Pankratov E.A., Nikiforov V.A.

The Tver State Technical University
Quay A.Nikitin, house 22, Tver, Russia
lagusseva@yandex.ru

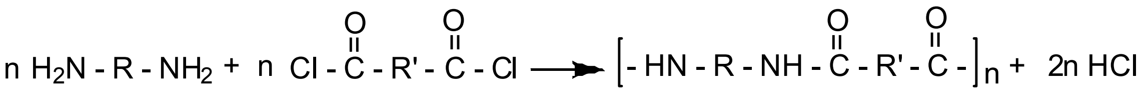
Reactionary casting of fibrids by the method of gas-fluid polycondensation is one of the most perspective and ecologically clean. Fibrids have anizometrichnoe texture with incorrect form, high specific surface and ability for binding together in the mass with the leaflike materials formation. That's why they are adjusted to the synthetic papers production and electrotechnical and constructional function, filter materials and elements, not weaved materials [1, 2].

The construction of reactor-fibridator was developed. It is vertical cylindrical reactor (pic. 1), which includes reaction chamber 5 and a gas-forming chamber located under it. The gas-forming chamber consists of sprayer blender 9 and evaporator-overheater 10. The reaction chamber is realized in different variants of basic design: with grate at the gas phase input (pic. 1) and non-grate one of confusor-diffuser type (pic. 2), sprayer and split way of liquid phase feed. It provides liquid-gas interface, diffusion of acidylable and acidylating monomers from volume towards phase interphase (reaction space), the chemical process of monomer polycondensation



1 – reaction chamber;
2 – sprayer blender;
3 – evaporator-overheater;
CA – dicarboxylic acid dichlorides;
HMDA – hexamethylenediamine

Pic. 1. The reactor-fibridator



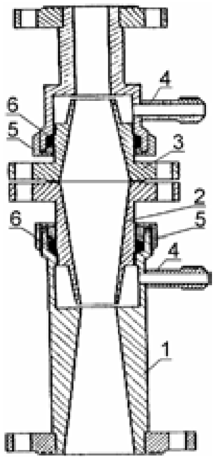
$$n\ H_2N - R - NH_2 + n\ Cl - \overset{\overset{\displaystyle O}{\|}}{C} - R' - \overset{\overset{\displaystyle O}{\|}}{C} - Cl \longrightarrow \left[- HN - R - NH - \overset{\overset{\displaystyle O}{\|}}{C} - R' - \overset{\overset{\displaystyle O}{\|}}{C} - \right]_n + 2n\ HCl$$

and neutralization of low-molecular product of polycondensation

$$HCl + NaOH \longrightarrow NaCl + H_2O\ ,$$

it also provides the fibrids molding from gel-like polymer firm during its creation in turbulazed three-phase foam conditions by means of shift voltage.

The engineering calculation of the generation gas-phase box and of the reactionary box of the reaktor-fibridator technique is developed.



1 – confusor of the first level; 2 – diffuser; 3 – confusor of the second level; 4 – choke of the fluid phase travel; 5 – press-ring; 6 – closure

Pic. 2. Two-phase confusor-diffuser reaction chamber

One of the main technological parameters, which defines foam hydrodynamic process regime and plant productivity, – linear speed of the gas-phase (w_g). The influence of the w_g on the yield polymer (ε), molecular weight (is expressed with the adduced ductility), grade degree of the polyamide fibrids 6T (polygexametilentereflamids) was experimental searched. Because the parameter «linear speed of the gas-phase» as criterion of the reactor-fibridator projecttion, which have different diameters and construction of the entering method of the gas-phase, is unusable, the analysis of the reactor equipment was conducted.

Optimal values of the hydrodynamic likeness criterion (Reinolds Re_r and Frud Fr_r) for the reactor-fibridators: without grill with the two-phase reactor cameras Re_r = 7000-9000, Fr_r = 8000-10000; with grills Re_r = 16000-20000, Fr_r = 1800-2200 were found. These criterion dependences help to model processes of the gas-fluid polycondensation by the synthesis of the fibrids 6T, which are flowed in the intensive foam regime, and by the given diameter of the equipment taking into account his construction characteristic and to define optimal linear speed and productivity of the equipment on the whole.

Reaktor-fibridator has small siye and high productivity G, which is defined with the formula: $G = 2{,}83 \cdot w_g \cdot d^2 \cdot C_{CA}^{g.ph} \cdot M \cdot \varepsilon, kg/h,$

(d – reactor-fibridator inside diameter, m; $C_{CA}^{g.ph}$ – molar concentration of the CA, mole/m^3; M – polymer segment molecular mass, g/mole).

The pilot plant was equipped by reactor-fibridators with inside diameter from 16 till 200 millimeter. More than 20 kinds of homo- and copolyamide fibrids were received.

References

[1]. V.A. Nikiforov, S.A.Zhizhilev, A.G. Mukhometzyanov, L.B. Sokolov, N.I. Gelperin, T.I. Nikitina, V.I. Rabinovich. Gaz/liquid interfacial preparation of poliamide fibrids. Patent 4396758 (USA).

[2]. V.A. Nikiforov, E.A. Pankratov, E.I. Lagusseva, A.V. Berezkin. Gas-liquid polycondensation. Tver, TSTU, 2004. 268 p.

ENHANCED YIELD OF DIETHYLCARBONATE VIA CATALYTIC ROUTE FROM CO_2 AND ETHANOL: SHIFTING OF THE EQUILIBRIUM BY A CHEMICAL WATER TRAP

<u>Leino E.</u>[1], Mäki-Arvela P.[1], Salmi T.[1], Murzin D.Yu.[1], Mikkola J.[1,2]

[1]Process Chemistry Centre, Åbo Akademi University, Biskopsgatan 8,
FI-20500 Turku/Åbo, Finland. E-mail: ewleino@abo.fi
[2]Department of Chemistry, Technical Chemistry, Chemical-Biological Center,
Umeå University, SE-90187 Umeå, Sweden.

Recently, substantial effort has been dedicated to the development of new synthesis methods based on CO_2 as a clean feedstock for organic carbonates. The obvious reason is their excellent properties and apparent commercial applications. Diethyl carbonate (DEC) is considered to be a better candidate for replacing methyl *tert*-butyl ether as an additive for gasoline than dimethyl carbonate (DMC) or ethanol. Furthermore, DEC is an environmentally benign and can be used as a feedstock in many industrial applications [1All the conventional production technologies raise problems such as the toxicity of phosgene, corrosion and low production rate. Thus, the straightforward catalytic synthesis of DEC starting from cheap, easy to handle and non-toxic carbon dioxide and ethanol $2\,C_2H_5OH + CO_2 \xrightleftharpoons{\text{cat.}} C_2H_5OCOOC_2H_5 + H_2O$ has recently become of great importance also due to the CO_2 utilization aspect.

The thermodynamics of DEC formation using ethanol and carbon dioxide as raw materials is not favorable, since the reaction does not occur spontaneously at room temperature ($\Delta_rG^{\varnothing}_{298K} = 35.85$ kJ/mol > 0). Therefore, an extremely high pressure is required for spontaneous reaction to occur. Moreover, the presence of co-produced water easily shifts the equilibrium towards the reactants. Thus, the main aim of this work was to investigate the performance of butylene oxide as a chemical dehydrating agent in combination with different catalysts in order to shift the equilibrium and achieve high yields of DEC.

The reaction was carried out in a stainless steel autoclave with an electric heater and a magnetic stirrer. The reactor was charged with 314 mmol of ethanol, 19 mmol of butylene oxide and 1 g catalyst and then pressurized with CO_2 (4.5 MPa initial CO_2 pressure) at room temperature, and thereafter heated to 170 °C. The reaction mixture was analyzed by means of gas chromatography (GC) (a capillary column

100 m x 250 µm x 0.5 µm, Agilent 122-10A6 DB-petro) equipped with a FID detector with helium being the carrier gas. Several catalysts i.e. $KCl/K_2CO_3/ZrO_2$, KCl/CeO_2, CeO_2 (commercial and in-house synthesized) and CeO_2-Mg (turnings) have been studied. The results revealed an 8-fold enhancement of DEC yield in the presence of butylene oxide in comparison to the synthetic method without any water removal (Table 1 entries 3 and 4). The conversion of ethanol and butylene oxide was 14 % and 96 %, respectively, confirming that the presence of a chemical dehydrating agent shifts the equilibrium in favour of DEC formation. The properties of the catalysts were evaluated by X-ray diffraction (XRD), nitrogen adsorption, temperature programmed desorption of CO_2 (TPD) and pyridine adsorption by Fourier Transform Infrared Spectroscopy (FT-IR).

Table 1. Catalyst screening results for direct synthesis of DEC from CO_2 and ethanol Conditions: 170 °C, 23 h, catalyst calcination temp. 600 °C, 314 mmol ethanol, 4.5 MPa initial CO_2 pressure, 1 g catalyst.

Entry	Catalyst	$\text{Pressure}_{\text{final}}$ (MPa)	DEC (mmol)
1	^{a} $KCl/K_2CO_3/ZrO_2$	10.4	—
2	^{b} CeO_2	9.7	0.05
3	^{c} CeO_2	12.6	0.28
4	^{c,d} CeO_2	11.0	2.36
5	^{c,d,e} CeO_2 − Mg (turnings)	10.9	1.99
6	^{c,d} KCl/CeO_2	9.9	0.68

[a] catalyst synthesized as in reference [2]
[b] cerium oxide synthesized (pH adjusted to 10 with NH_4OH) and calcined at 800 °C
[c] cerium oxide nanopowder (Sigma-Aldrich)
[d] reaction with 19 mmol of butylene oxide
[e] added 0.5 g of Mg (turnings)

In the presentation the reaction network, the properties of the best performing catalyst and the optimal reaction conditions will be discussed.

References

[1]. M.A. Pacheco and C.L. Marshall, *Energy Fuels*, 1997, 11, p. 2.

[2]. V. Eta, P. Mäki-Arvela, J.-P. Mikkola, K. Kordas, D. Yu. Murzin and T. Salmi, *Progress in Heterogeneous Catalysis* (ed. Marmaduke D.L.), Nova Publishers New York, 2008, p. 135.

COMPETITIVE ADSORPTION OF FISHER-TROPSCH MIDDLE DISTILLATE LINEAR PARAFFINS ON AMORPHOUS SILICA-ALUMINA ERS-8

Li B.[1], Denayer J.F.[2], Calemma V.[3]

[1]Department of Chemical Engineering, Vrije Universiteit Brussel, Pleinlaan 2,
B-1050 Brussel, Belgium. E-mail: benli@vub.ac.be
[2]Department of Chemical Engineering, Vrije Universiteit Brussel, Pleinlaan 2,
B-1050 Brussel, Belgium. E-mail: joeri.denayer@vub.ac.be
[3]Eni S.p.A Divisione Refining & Marketing - Centro Ricerche di San Donato Milanese,
Via Maritano 26, 20097 San Donato Mil. se, Milan, Italy.
E-mail: vincenzo.calemma@eni.com

Introduction Fisher–Tropsch (F–T) products are essentially made up of *n*-paraffins together with small fraction of alcohols and olefins. The poor cold flow property of the F–T middle distillate limits their direct use as fuel. To improve both yield in middle distillate and cold flow property, the waxes are subjected to hydroconversion where the heaviest fraction is hydrocracked to lighter compounds and isomerized to improve the cold flow property [1]. The catalytic hydroconversion of F–T waxes involves several steps [2], and it has been addressed that both reaction rates and selectivities of the different paraffins constituting the reaction mixture can be strongly affected by their adsorption behaviors in the pores.

In this work, competitive adsorption of binary *n*-paraffin mixtures on the porous material ERS-8 was studied in liquid and dense vapor phase with the breakthrough method. Equilibria constants of vapor-liquid phase, vapor phase adsorption and liquid phase adsorption were modeled by thermodynamic calculation.

Results The effect of temperature and pressure on competitive adsorption was determined using binary mixtures of nC20 and nC30 dissolved in *iso*-octane. At 25 °C and at 150 °C, no preferential adsorption is observed, both components elute simultaneously. However, from 200 °C components are separated and longer component are retained much longer. This tendency becomes more pronounced with increasing temperature. When pressure is increased, the difference in adsorption between short and long chain decreases again. The breakthrough time of the heaviest paraffin in the mixture clearly increases with chain length. This, the selectivity depends on pressure and temperature; strong competition occurs in vapor phase conditions whereas short and long chains adsorb equally in full liquid conditions.

A model was developed to calculate vapor and liquid phase adsorption properties as function of chain length. It can be seen in Figure 1 that equilibria constants of vaporization and gas phase adsorption vary exponentially with carbon number, but in an opposite way. As a result, the liquid phase adsorption equilibrium constant, which can be calculated as the product of equilibria constants of vaporization and gas phase adsorption, is only weakly dependent on chain length.

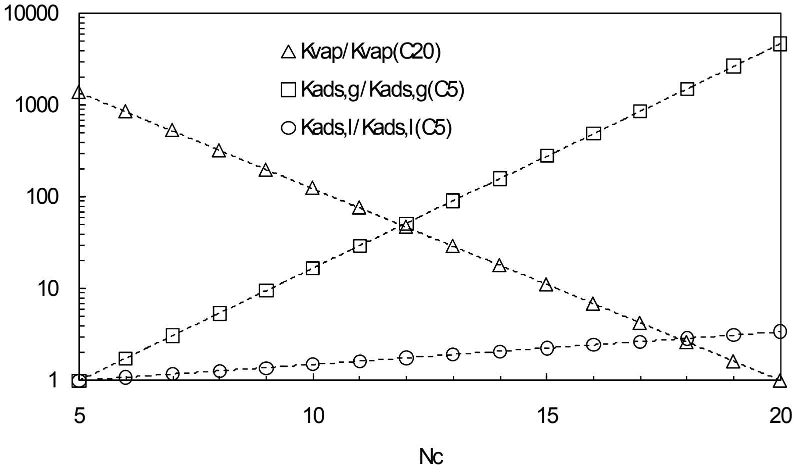


Fig.1. Ratio of equilibrium constants for adsorption from vapor and liquid phase plotted as a function of carbon number on ERS-8 at 250 °C.

Conclusion Both the adsorption capacity and the selectivity are strongly temperature and pressure dependent. At low temperature and high pressure, all *n*-paraffins are adsorbed equally. With increasing temperature and decreasing pressure, the density of the bulk phase decreases, and a transition from a pure liquid paraffin stream to a dense vapor stream occurs. In such conditions, longer *n*-paraffins are adsorbed preferentially compared to the shorter *n*-paraffins. The selectivity increases with increasing difference in chain length between the adsorbing *n*-paraffins.

References

[1]. Pellegrini, L, A.; Gamba, S.; Calemma, V. Equilibrium Constants for Isomerization of n-Paraffins. Ind. Eng. Chem. Res., **2007**, 46, 5446.

[2]. Calemma, V.; Peratello, S.; Perego, C. Hydroisomerization and Hydrocracking of Long Chain n-Paraffins on Pt/amorphous SiO2-Al2O3 Catalyst. App. Catal .A, **2000**, 190, 207.

Acknowledgements

This research is financially and substantially supported by Eni S.p.A, Refining & Marketing Division, Italy.

PP-II-26

INFLUENCE OF CHEMICAL-ENGINEERING SYSTEM STRUCTURE ON EFFICIENCY OF PENTANE-HEXANE FRACTION ISOMERIZATION PROCESS

Litvak E., Kravtsov A., Ivanchina E., Chekantsev N.

Tomsk Polytechnic University, Tomsk, Russia, e-mail: litvak_egor@mail.ru

Decrease of aromatic hydrocarbons content, especially benzene, in automobile fuels with simultaneous maintenance of octane number becomes an urgent problem in connection with the future transition of Russian oil-refining industry to the production of motor gasoline satisfying the requirements of «Euro-3» and «Euro-4» standards. It is well known that catalytic reforming, which products are the main sources of aromatics, remains traditionally the key process of straight-run petrol conversion in Russia. The catalytic isomerization of light alkanes is of the most interest in this context, it makes it possible to obtain high-octane component of automobile gasoline with minimum benzene hydrocarbons content.

Octane number of isomerizate, along with other factors, is determined by selection of process flow scheme. Different schemes of unreacted normal alkanes recirculation are used for the purpose of conversion level increment.

Objective of research is to determine the influence of chemical-engineering system configuration on efficiency of pentane-hexane fraction isomerization process. For this purpose computation of isomerizate composition and its octane number for different schemes was carried out with the support of computer simulation program «Isomer» developed by us. The following process schemes were compared:

- One-pass scheme;
- Scheme with recirculation of n-hexane and methylpentanes;
- Scheme with recirculation of n-pentane, n-hexane and methylpentanes;
- Scheme with preliminary disengagement of isopentane from feedstock and recirculation of n-pentane, n-hexane.

The reactor block of installation L-35-11/300 was taken as a basis for the calculations, catalyst – SI-2. Technological conditions of the process were invariable and were as follows: temperature in the first, second and third reactor – 133 °C, 146 °C, 156 °C, respectively; pressure – 2.6 MPa; feedstock flow rate – 90 m^3/h; hydrogen gas flow rate – 24957 m^3/h.

The results of calculations of octane number and other factors for the various technological schemes of isomerization process are presented in Table 1.

Table 1. Comparison of schemes of the isomerization process: (1) one-pass scheme, (2) scheme with recirculation of n-hexane and methylpentanes, (3) scheme with recirculation of n-pentane, n-hexane and methylpentanes, (4) scheme with preliminary disengagement of isopentane from feedstock and recirculation of n-pentane, n-hexane

Factor	**1**	**2**	**3**	**4**
Octane number of isomerizate (research method)	79.91	88.86	94.06	88.03
Content of isoalkanes in isomerizate, % wt.	46.62	71.49	87.26	63.54
Comparative production rate, %	100	62	58	82
Ratio of recycle stock flow rate to clean feed	–	0.61	0.72	0.35
∆ON, octane-ton	13.35	13.8	15.95	17.61

Use of schemes with recirculation leads increase in octane number of isomerizate on the one hand to, and to decrease in plant productivity on the other, the index ∆ON was introduced for correct comparison. It is the growth of octane number – an indicator that takes into account the capacity of installation and the octane number of the product and clean feed:

$$\text{ДON}=\frac{(ON_2\text{-}ON_1)\text{Ч}G}{100},$$

where ON_2 and ON_1 – octane numbers of isomerizate and clean feed, respectively; G – comparative production rate.

Summary

The highest octane number of isomerizate is observed when using the scheme with recirculation of n-pentane, n-hexane and methylpentanes. The octane number in this case is 94.06 points if full separation of n-pentane, n-hexane and methylpentanes from product is occurred. However, octane number growth is 15.95 octane-tons.

As a result of using the scheme with recirculation of n-hexane and methylpentanes obtained isomerizate has octane number of 88.86 points (with the full separation of n-hexane and metilpentanes). In this case, octane number growth is 13.8 octane-tone.

Application of the scheme with preliminary disengagement of isopentane from feedstock and recirculation of n-pentane, n-hexane gives an isomerizate with octane number of 88.03 points (with the full disengagement of isopentane from feed and n-pentane and n-hexane from product). Increase of octane-tones reaches a maximum value among the analyzed schemes – 17.61.

Using of one-pass scheme octane number of isomerizate is 79.91 points while the growth of octane-tons – 13.35.

PP-II-27

EFFICIENT OXYGENATION OF ALLYLIC COMPOUNDS BY SINGLET OXYGEN IN MICROSTRUCTURED REACTORS

Loponov K.[1], **Malkov A.**[2], **Lapkin A.**[1]

[1]*School of Engineering, University of Warwick, k.n.loponov@warwick.ac.uk*
[2]*Department of Chemistry, Loughborough University*

Oxyfunctionalization of allylic substrates by singlet oxygen ($^1O_2$) is a highly versatile synthetic method. For example, terpene-derived chiral ligands proved to be successful in a number of metal-based and metal-free catalytic transformations [1]. The key step for the synthesis of these catalysts is $^1O_2$ mediated conversion of α-pinene to pinocarvone. Another example is stereoselective photooxygenation of aromatic chiral homoallylic alcohols (ACHA), which may be further employed in the syntheses of important natural products, such as antibiotic showdomycin, or natural (pseudouridine) and artificial nucleobases.

The most frequently used method of $^1O_2$ generation in solution is photosensitized energy transfer from the photo-excited states of dissolved organic dye molecules to O_2. The process involves bubbling oxygen through the illuminated reaction mixture in a batch photoreactor and requires up to two days for completion on a several grams scale. Scaling up this protocol is limited by the available equipment due to inefficient light utilisation and hazards associated with unattended use of O_2. Moreover, in most cases the sensitizers are not reusable due to the complexity of separating them from the homogeneous reaction mixture. Microstructured reactors with the unique features of microchannels such as short molecular diffusion distances, excellent heat-transfer characteristics, and large surface-to-volume ratios, allow safe exploitation of explosive processes [2]. Better light penetration through the entire microchannel depth and spatial uniformity of illumination of the reaction medium provide more efficient light utilisation. Furthermore, once optimized, the process can be easily scaled up by the ‘numbering up’ of the microreactor units. In addition, problems related to recycling of the sensitizers can be overcome by immobilisation of dyes on the surface of microchannels.

Our work is aimed at developing the scalable microstructured reactor unit for efficient $^1O_2$ mediated oxyfunctionalization of allylic compounds useful for the synthesis of important chemicals.

In our study we tested anodically bonded glass-to-silicon flat microstructured reactor with meandering reaction channel attached to metal plate heat exchanger in the oxygenation of α-pinene by $^1O_2$ (Figure 1). We used continuous and recirculating modes of reaction and two different approaches to O_2 saturation (O_2 pre-saturation of reaction mixture and segmented gas-liquid flow in microchannel). We analyzed the influence of residence time, O_2 pressure, sources of light (524 or 416 nm LED arrays, Xe arc lamp), different sensitizers (tetraphenylporphine, Rose Bengal and tetra(4-hydroxyphenyl)porphine) and solvents (dichloromethane, ethanol) on the conversion of α-pinene to pinocarvone. Ferrioxalate actinometry was used to quantify the efficiency of light absorption and quantum yields of reaction. The optimal parameters found at this step were applied in the stereoselective oxygenation of ACHA by $^1O_2$. Microstructured reactor allowed us to increase the conversion while distribution of the products was shifted towards the desired stereoisomer owing to directing influence of the protecting group on alcohol. Finally, we modified the walls of silicon microchannel with covalently attached tetra(4-hydroxyphenyl)porphine and compared the results of photooxygenation in dye immobilized microreactor with these obtained earlier in homogeneous photooxygenation.

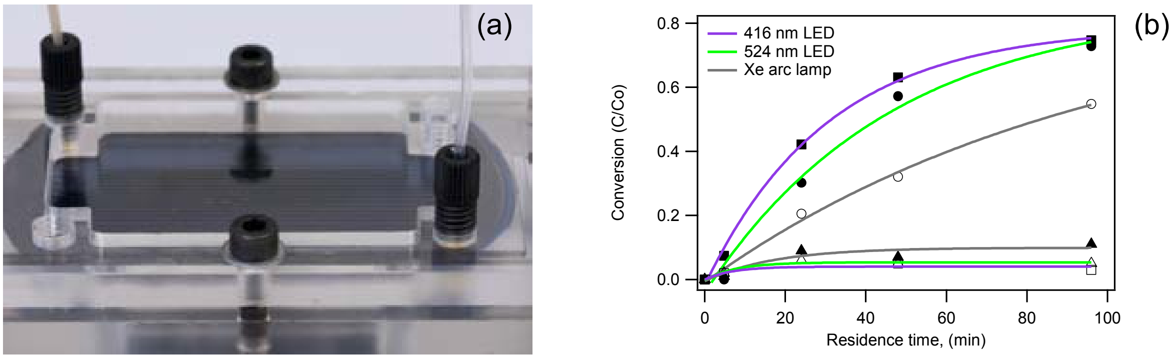


Figure 1. (a)-photo of glass-silicon microstructured reactor; (b)-conversion of α-pinene to pinocarvone in ethanol. ■, ●, and ○-tetra(4-hydroxyphenyl)porphine, ▲, Δ, and □-Rose Bengal, green-524 nm LED, violet-416 nm LED, black-Xe arc lamp.

References

[1]. Malkov A.V., Westwater M-M., Gutnov A., Ramírez-López P., Friscourt F., Kadlčíková A., Hodačová J., Rankovic Z., Kotora M., Kočovský P., New pyridine N-oxides as chiral organocatalysts in the asymmetric allylation of aromatic aldehydes, Tetrahedron, **2008**, 64, 11335–11348.

[2]. K. Jahnisch, V. Hessel, H. Lowe, M. Baerns, Chemistry in Microstructured Reactors, Angew. Chem. Int. Ed., **2004,** 43, 406-446.

Acknowledgements

We gratefully acknowledge the EPRSC for funding this project, B. Goller and M. Kabeshev for their help during the work and discussion of the results.

CATALYTIC SYSTEMS OF HYDROGEN PRODUCTION FOR FUEL-CELLS WITH A REMOVAL OF CARBON DIOXIDE FROM GAS MIXTURE IN SITU

Lukyanov B.N., **Lysikov A.I., Okunev A.G.**

Boreskov Institute of Catalysis SB RAS, Prosp. Akad. Lavrentieva, 5,
Novosibirsk 630090, Russia

Catalytic production of hydrogen from hydrogen-containing sources such as water, natural gas, oil, coal, biomasses, timber, and industrial waste is promising for fuel-cell based power generation [1,2]. Utilization of hydrogen permits one to avoid the problem of direct electrification, which is accompanied by large electric losses and impossibility of energy storage. Besides, hydrogen recovery provides no harmful substances as methane or carbonic acid exhausts. The value of hydrogen energy per mass unit (120.7 MJ kg^{-1}) is higher than those of the known organic fuels. Note that the hydrogen meant for fuel cells including a proton-exchange membrane should have high purity grade and CO concentration not higher than 10 ppm.

In this report the main catalytic processes and types of fuels used in hydrogen production for fuel cells are described. The main attention paid to the single-step fixed bed sorption enhanced reforming (FBSER) as a primary method of hydrogen production. FBSER include a simultaneous reforming of hydrocarbon fuel and a sorption of side product - CO_2 [3-5]. The types of adsorptive reactors which used in a pressure and thermal swing or membrane separating systems are observed. The description of new regenerative membrane systems as Hybrid Adsorbent-Membrane Reactor (HARM) and Air Revitalization System (ARS) which used in space flights are given. The different aspects of FBSER including it a technical realization in reactors with moving or fixed beds are analyzed. The high-temperature CO_2 sorbents and catalysts used in adsorptive reactors are observed. It was shown that the synthetic porous Ca-based sorbents have a high dynamic capacity which is stable in sorption-enhanced reforming. The prospects of FBSER in hydrogen energy are analyzed. The work includes more than 90 references.

References

[1]. Ogden D., Great Expectations. // V mire nauki, **2007** Vol. 1. P.69 (in Russian).

[2]. Methanol or Hydrogen. Outlook for Development of Fuel Cells in the World. // Chemistry and Business. **2004** Vol. 3, № 61. P. 63.

[3]. Harrison D. Sorption-Enhanced Hydrogen Production: A Review. // Ind. Eng. Chem. Res. **2008.** Vol. 47. P. 6486.

[4]. Lukyanov B.N., Lysikov A.I., Okunev A.G. Catalytic systems of hydrogen production for fuel-cells with a removal of carbon dioxide from gas mixture in situ. // Chem. Sustain. Dev. **2010.** Vol. 2. in press.

[5]. Lysikov A.I., Lukyanov B.N., Okunev A.G. Sorption enhanced reforming: reactors, sorbents, catalysts. // Chem. Sustain. Dev. **2010.** in press.

OZONE-DESTRUCTION REACTOR BASED ON FOAM POLYURETAN WITH PEROVSKIT CATALYTIC LAYER

Makarov A.A.[1], Makarov A.M.[1], Ostroushko J.J.[2]

[1]*ZAO ECAT, Perm, Russia, mak_perm@mail.ru*
[2]*Ural state university, Ekaterinburg, Russia*

Free radical reactions of destruction of ozone in the gaseous phase which began in the gas mixture continue after the air passes the partition on the highly-developed HPHM surface with catalytic cover based on aluminum and rare-earth metal oxides.

High-porosity permeable cellular polyuretan represent a new type of structures having unsurpassed porosity, permeability and cohesion. The combination of heterogeneous catalysis at low-temperature and foam structure has allowed creation ofcompact high-efficiency ozone-destruction reactor.

Highly permeable structure of HPCM effectively dissipates heat and removes generated ozone in a gas stream. Computer simulation of heat-exchange, flow regime, temperature and pressure is carried out with the use of a finite elements method.

Results of simulation have allowed to optimize a design and to improve efficiency of destruction ozone in air.

PP-II-30

MODELING OF METHANE STEAM REFORMING PROCESS IN POROUS CATALYST

Mehdizadeh H. and **Sadeghi M.T.**

Process Simulation and Control Research Lab., Chemical Engineering College, Iran
University of Science and Technology (IUST), Narmak 16846, Tehran, Iran.
E-mail: sadeghi@iust.ac.ir

ABSTRACT

Hydrogen is widely used as feedstock of various chemical processes, petroleum industries and petrochemical plants. It is generally produced via steam reforming of natural gas at oil refineries. The reforming units are basically containing burners and fixed bed reactors [1-3] packed by nickel catalyst type particles. The packed bed tubes are exposed to significant axial temperature gradients due to the high heat input on the tube's wall [2]. In previous works, it has been found that by increasing the lumen pressure, methane conversion increases in the membrane reactor [4]. Moreover, the velocity and heat transfer coefficient have influence on methane conversion [5]. The intraparticle temperature differences are small compared to external temperature differences at high fluid temperature [6].

In this work, a two-dimensional model of fixed bed reactor for the catalytic methane steam reforming process is developed in order to investigate the effect of different parameters on axial temperature and methane conversion. Partial differential equation describing conversion laws for mass, energy and momentum transfers were solved in order to study the heat transfer and fluid flow in the system. The kinetics of methane reforming and the reactions mechanism were obtained from Hou and Hughes [7].

Influences of the inlet temperature on methane conversion at constant pressure as well as inlet pressure on the methane conversion at constant temperature are investigated. The results show that increasing the inlet temperature leads to increase of methane conversion however, the temperature differences along the reactor is also reduced. It was found that the methane conversion decreases with increasing inlet pressure while the axial temperature profile is increased along the reactor.

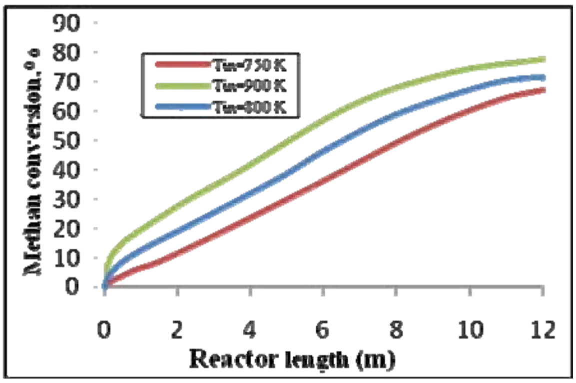


Fig. 1. Axial profile of methane conversion (%) with varying inlet temperature

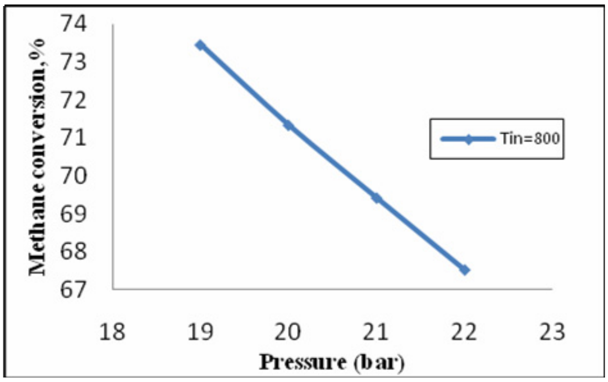


Fig. 2. Methane conversion (%) versus reactor pressure

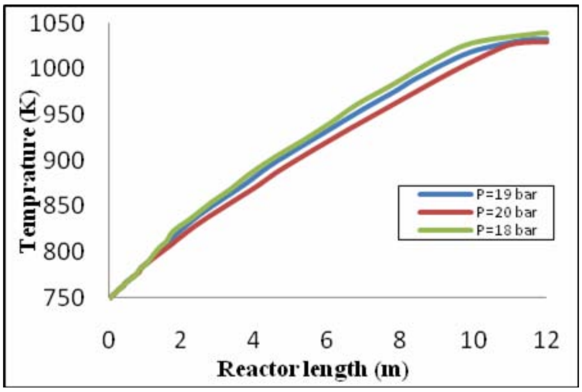


Fig. 3. Temperature profile in the reactor at different pressure

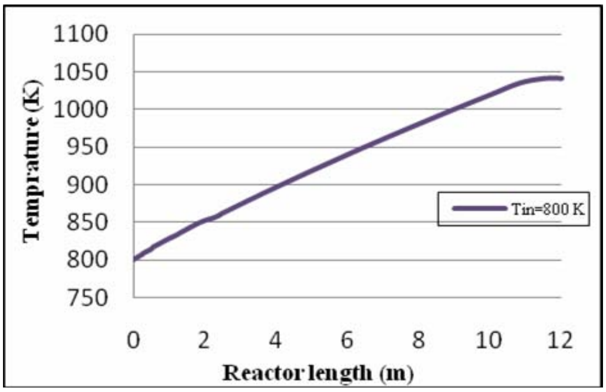


Fig. 4. Axial temperature profile in the reactor

Table 1. Temperature differences along the reactor at various inlet temperatures

T_{in}	T_{out}	ΔT
750 K	1032.8 K	282.8
800 K	1042.3 K	242.3
850 K	1049.8 K	199.8

Reference:

[1]. Chen, Z.; Prasad, P.; Yan, Y.; Elnashaie, S. Simulation for reforming of natural gas with oxygen input in novel membrane reformer. Fuel Processing Technology. **2003**, 83, 235-252.

[2]. Pedernera, M.N.; Piña, J.; Borio, D.O.; Bucalá, V. Use of a heterogeneous two-dimensional model to improve the primary steam reformer performance. Chemical Engineering Journal. **2003**, 94, 29-40.

[3]. Huang, T.J.; Yu, T.C.; Jhao, S.Y. Weighting Variation of Water-Gas Shift in Steam Reforming of Methane over Supported Ni and Ni-Cu Catalysts. Ind. Eng. Chem. Res. **2006,** 45, 150-156.

[4]. Gallucci, F.; Paturzo, L.; Basile, A. A simulation study of the steam reforming of methane in a dense tubular membrane reactor. International Journal of Hydrogen Energy. **2004**, 29, 611-617.

[5]. Grevskott, S.; Rusten, T.; Hillestad, M.; Edwin, E.; Olsvik, O. Modelling and simulation of a steam reforming tube with furnace. Chemical Engineering Science. **2001**, 56, 597-603.

[6]. Levent, M.; Budak, G.K.; Karabulut, A. Estimation of concentration and temperature profiles for methane-steam reforming reaction in a porous catalyst. Fuel Processing Technology. **1998**, 55, 251-263.

[7]. Hou, K.; Hughes, R. The kinetics of methane steam reforming over a Ni/a-Al2O catalyst. Chemical Engineering Journal. **2001**, 82, 311-328.

MATHEMATICAL MODELING OF REACTIVE DISTILLATION SYNTHESIS OF MTBE

Mityanina O.E., Samborskaya M.A., Kravtsov A.V.

Tomsk Polytechnic University, Tomsk, Russia, e-mail: elvoreth@mail.ru

During the last three decades carrying out a chemical reaction combined with the separation of reactive mixture in the same apparatus is becoming more and more significant for chemical industry. Organization of processes by this way has hydrodynamical and kinetical advantages. Besides, it often turns out that a combined process is the most simple and economically sound [1].

There is a number of technological limitations, preventing the reactive distillation processes. The main limitations are the temperature limitation (chemical stage of the process carries out beyond the range of components boiling points) and time limitation (duration of the chemicall reaction can not be above the dwelling time in column), also, both reagents and products must have different boiling points [2].

However, the reactive distillation concept allows to decrease capital outlays and energy expenditure. In particular, the widest used reactive distillation process is the producing of methyl-tert-butyl ether (MTBE), ethyl-tert-butyl ether (ETBE) and other etherification processes [3].

Due to interaction between chemical reaction and mass-transfer, combined processes can show extremely non-linear behavior and steady state multiplicity. Thus, the main feature of combined processes is the presence of non-linear members in mathematical model. The non-linearity emanates from non-linear dependency of reaction rate from temperature and concentration. Since these etherification processes are characterized by high nonideality of behavior, the chemical reactions are defined with respect to activity.

This fact significantly complicates dynamical research and control problem in practice. Thus, the creation of optimal control strategy based on unsteady mathematical models, considering physical and chemical properties of combined process is a very actual object.

VLE calculations in the system, done by some researchers within the bounds of modeling, played secondary role. Thus they were carried out in the narrow range of process-dependent parameters and concentrations, which is not enough to obtain reliable correlations suitable for control purposes. The aggregation of n-butene and isobutylene in butene fraction is reasonable from the simplification of dynamic model point of view, because n-butene does not participate in the chemical reaction. However, presence of n-butene in reactive mixture has significant influence on phase equilibrium of the system. In view of the fact that the ratio isobutylene : n-butene in the reactive mixture reaches 1 : 3, the influence of n-butene on VLE can significantly change the process in general. We suppose that the research of n-butene concentration influence on the activity coefficients is the most interesting.

Hence, one of the aims of this work is researching VLE in “Isobutylene – n-butene - methanol - MTBE” system and obtaining the empiric dependencies used for the combined processes control algorithms (Table 1).

Table 1 – Empirical correlations between the activity coefficients and the temperature and the concentration of all components in “Isobutylene – n-butene - methanol - MTBE” system.

	R2
$\ln\gamma^{i-bu} = -0.275x^{n-bu} + 0.585x^{MeOH} - 1.543x^{MTBE} + 0.019T - 6.377$	1
$\ln\gamma^{n-bu} = -0.29x^{n-bu} + 0.56x^{MeOH} - 1.536x^{MTBE} + 0.0185T - 6.266$	1
$\ln\gamma^{MeOH} = 15.12x^{i-bu} + 15.22x^{n-bu} + 13.69x^{MeOH} + 12.7x^{MTBE} - 0.015T - 7.4$	0,9939
$\ln\gamma^{MTBE} = 3.53x^{i-bu} + 2.64x^{n-bu} + 3.35x^{MeOH} + 1.42x^{MTBE} + 0.0007T - 5.3$	0,9902

This result is used for dynamical mathematical model of the process, which is consist of MEH equations. The model enables to provide quality control, and prediction of process behavior under disturbances.

References

[1]. Gruner S. et al. Nonlinear control of a reactive distillation column // Control Engineering Practice 11. – **2003**;

[2]. Yang Bolun et al. Multiplicity Analysis in Reactive Distillation Column Using ASPEN PLUS // Chinese J. Chem. Eng. - **2006**;

[3]. Singh B.P. Steady State Analysis of Reactive Distillation Using Homotopy Continuation // Chemical Engineering Research and Design. – **2005**.

PP-II-32

EFFICIENCY IN PHOTOCATALYTIC REACTORS: MODELING OF RADIATION ABSORBED BY THE CATALYST

Jesus Moreira[1], **Benito Serrano**[2], **Aaron Ortiz**[1], **Hugo de Lasa**[1]

[1]*The University of Western Ontario, London, Ontario., Canada, jmoreira@uwo.ca*
[2]*Universidad Autónoma de Zacatecas, Mexico*

Abstract

Photocatalytic reactions are the result of the interaction of light with a solid semiconductor generating e^-/h^+ pairs which are responsible for the degradation of organic and inorganic compounds [1]. Several efficiency definitions in photocatalytic reactors are found in the literature; in all cases, efficiency determination involves a key variable, the rate of photons absorbed by the photocatalyst, which is found from the local volumetric rate of energy absorption (LVREA). An accurate evaluation of LVREA is fundamental in the design and rating of photoreactors, and its estimation involves the solution of the Radiative Transfer Equation (RTE). Stochastic methods, such as Monte Carlo method (MCM), can be implemented with advantage over deterministic methods in finding the LVREA [2]. A macroscopic radiation balance (MRB) can be performed combining radiometric measurements with a radiation balance to experimentally determine the radiation absorbed by the photocatalyst inside the photoreactor [3]. In the present study, the LVREA for a photocatalytic reactor is simulated by using MCM for two TiO_2 catalysts (DP25 and Anatase). The experimental LVREA was found for DP25 and Anatase catalysts applying a MRB to a control volume in the photoreactor with boundaries containing the slurred TiO_2 catalyst. In the simulations, the averaged absorption and scattering coefficients as well as their spectral distribution were used. Other parameters were also considered: the probability of photon absorption by the catalyst and the probability of radiation absorption by the internal Pyrex glass tube. The Henyey-Greenstein phase function was adopted to represent forward, isotropic and backward scattering modes. It was also assumed that the UV lamp reflects all the back-scattered photons by the slurred medium. Comparison of light absorption and forward-scattering radiation from experimental MRB and MCM showed a good agreement when the spectral distribution for the absorption and scattering coefficients were used (see Figure 1). In all the simulations, isocratic scattering rendered better results when compared with experimental values.

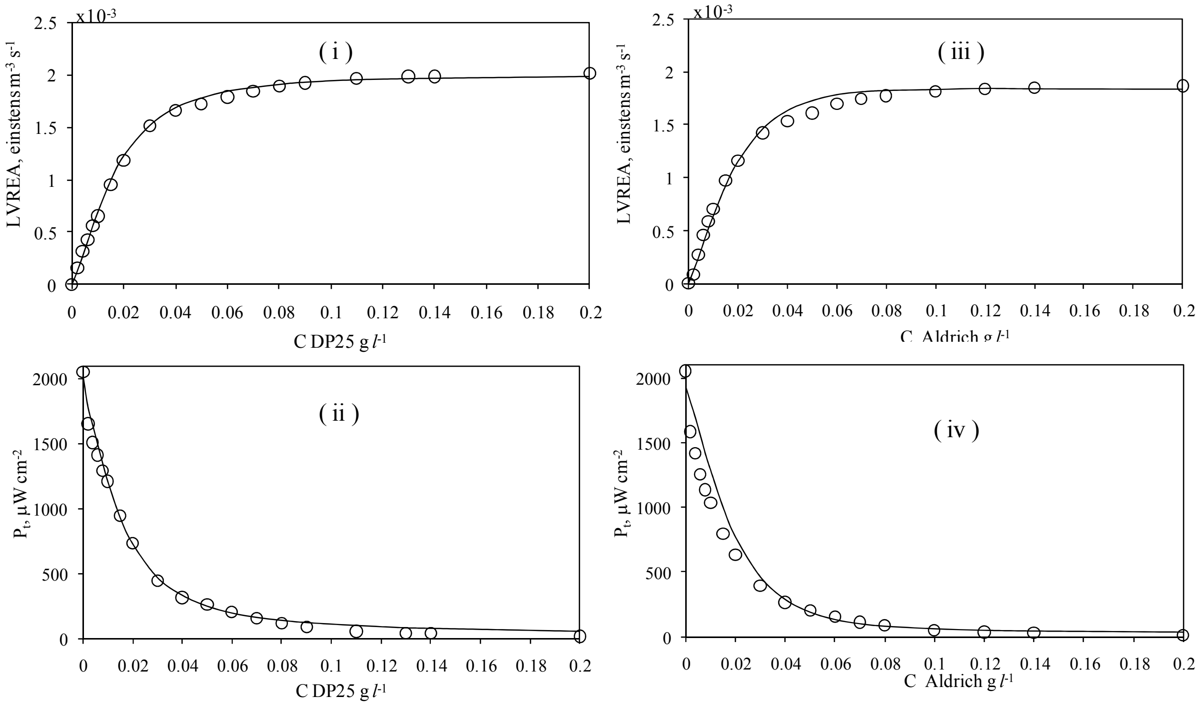


Figure 1. Experimental LVREA and transmitted radiation (P_t) and the comparison with MC simulations (○) Experimental results, (—) MC simulation. (i) LVREA for DP25, (ii) P_t for DP25, (iii) LVREA for Aldrich and (iv) P_t for Aldrich.

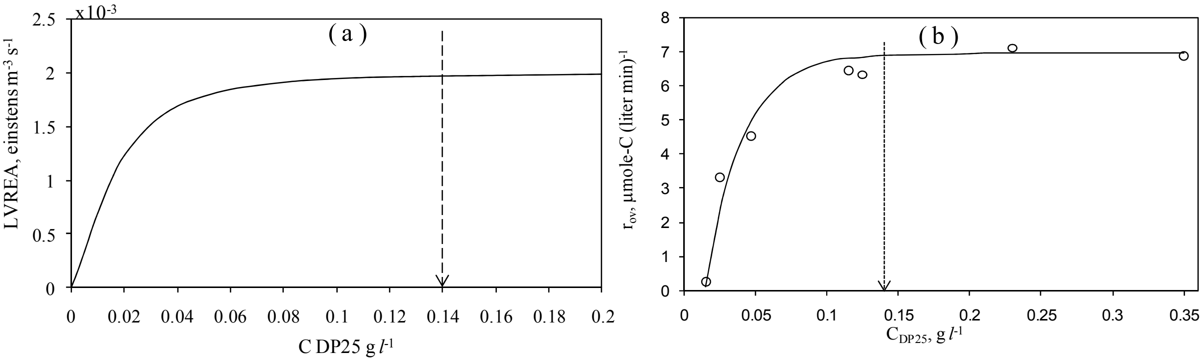


Figure 2. (a) LVREA inside the Photoreactor vs. DP25 loading. (b) Overall reaction rate for phenol degradation vs. DP25 concentration.

Additionally, MC simulations allowed the determination of the *optimal catalyst concentration* inside the reactor. It can be seen in Figure 2 that the maximum reaction rate for phenol degradation occurs at the maximum LVREA found with MCM. MCM is an efficient tool in finding the LVREA for a photocatalytic reactor.

References

[1]. de Lasa, H.; Serrano, B.; Salaices, M. Photocatalytic Reaction Engineering**.** *Springer: New York, 2005.*

[2]. Pareek, V.; Ching, S., Tade, M.; Adesina A. A. Light intensity distribution in heterogeneous photocatalytic reactors. *Asia-Pac. J. Chem. Eng.* **2008**, 3, 171.

[3]. Salaices, M.; Serrano, B.; de Lasa, H. I. Photocatalytic Conversion of Organic Pollutants Extinction Coefficients and Quantum Efficiencies, *Ind. Eng. Chem. Res.* **2001**, 40, 5455.

MODELLING THE EFFECT OF VAPOUR LIQUID EQUILIBRIUM ON FISCHER TROPSCH SYNTHESIS PRODUCT DISTRIBUTIONS FOR CONTINUOUS, WELL-MIXED SLURRY REACTORS

Mthombeni B.[1], **Möller K.P.**[2]

[1,2]*Department of Chemical Engineering, Upper Campus, University of Cape Town,*
Rondebosch, 7701, South Africa, Tel: +27216502518, Fax: +27216505501
[1]*E-mail: bongani.mthombeni@uct.ac.za;*
[2]*E-mail: klaus.moller@uct.ac.za*

Fischer Tropsch Synthesis (FTS) is the conversion of syngas (CO and H_2) to cleaner liquid transportation fuels. The modelling of such a supercritical, highly non-ideal, multi-component system requires the detailed knowledge of the reaction mechanism, reaction kinetics, phase equilibrium and reactor technology. Olefin readsorption has been a controversial matter in FTS literature with the observation of more than one alpha-value being accounted to it. The objectives of this work were to: develop a complete FTS model, predict the hydrocarbon product distribution, determine what effect Vapour-Liquid Equilibrium (VLE) has on the product distribution, selectivity and kinetics, and determine whether the deviations from the 'ideal' Anderson-Schulz Flory (ASF) distribution can be attributed to VLE.

Two models were developed for FTS in a well-mixed, continuous slurry reactor: a ***single-phase model*** and a ***two-phase model***. In the two-phase model, a different approach to the conventional product distribution model was taken whereby the model was developed considering the phase equilibrium and reaction kinetics of the system simultaneously. The kinetic model was developed using elementary reaction steps for the olefins and paraffins based on the species' activities, a function of the species' partial molar fugacities. For the single-phase model, the activity was considered as the ratio of the species partial pressure to the standard pressure. The reactor is assumed to behave as an ideal, well-mixed, continuous flow reactor with no heat or mass transfer limitations. The dynamic, transient, continuous mass balances were written for all species and their intermediates, leading to a system of (7N+10) Differential Algebraic Equations (DAE's) for the two-phase system that considered VLE, and (5N+7) DAE's for the single-phase system that didn't consider VLE, where N is the maximum carbon number, N = 60. The product distribution, selectivity, kinetics, ratio of olefin:paraffin reaction rates , and steady state results of the two models were compared, where the operating conditions and kinetic parameters for both models were the same, the only difference being the formulation of the activity.

The olefin readsorption was considered by initially setting a low specific reaction rate constant ($k6_r$) for the olefin formation reverse reaction and increasing it for olefin readsorption to be significant.

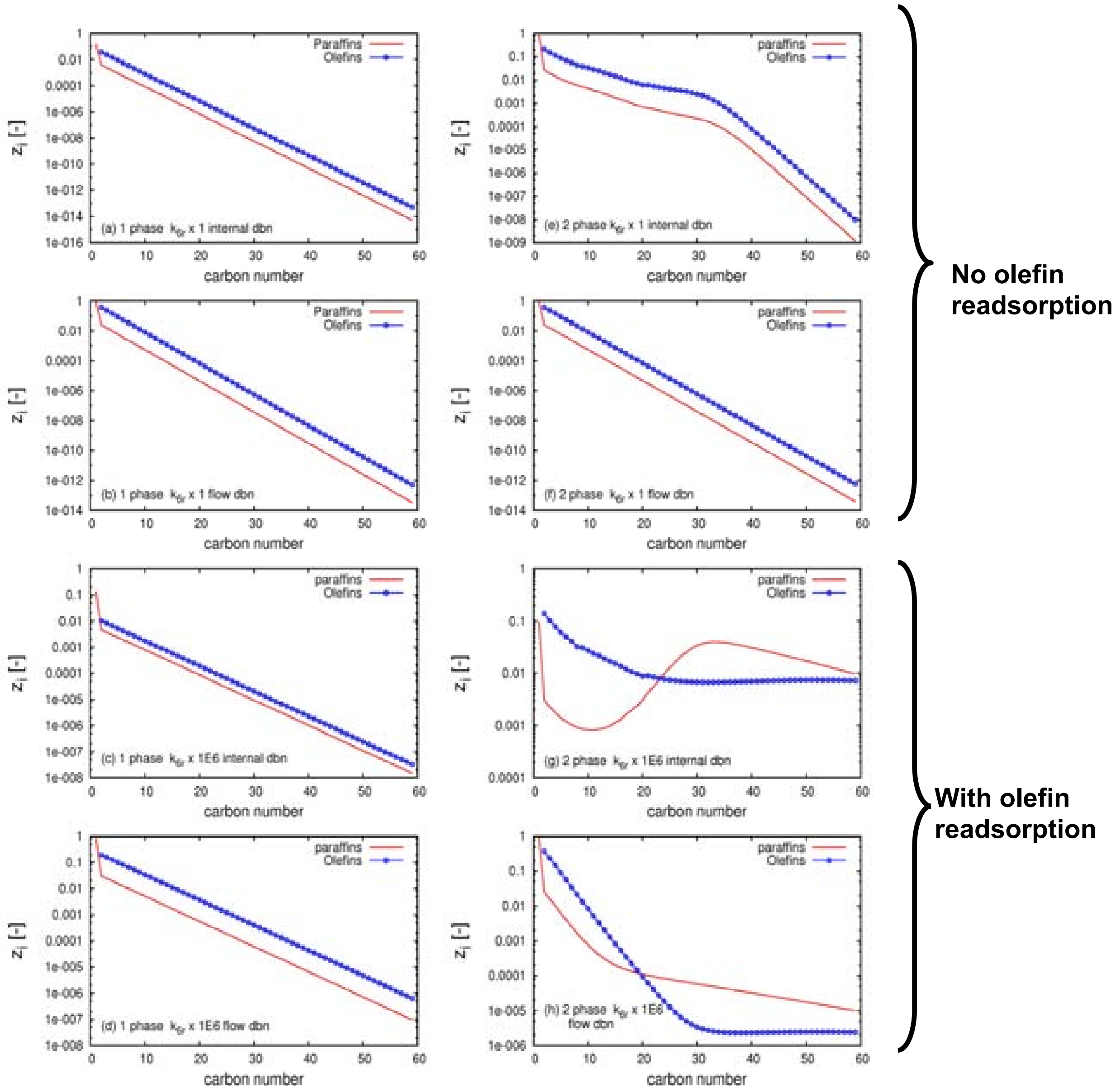


Figure 1: Hydrocarbon distribution inside the reactor and the flow distribution leaving the reactor for both the single-phase (a, b, c, d) and the two-phase models (e, f, g, h) for no olefin readsorption, and considering olefin readsorption.

As shown in Figure 1, for the single-phase model, irrespective of olefin readsorption a single α-value is observed inside the reactor and for the external flow distribution, as for a classical ASF distribution. For the two phase model, with no olefin readsorption, due to the internal dynamics of the system and the phase split, two α-values are observed inside the reactor; an "ASF"-like distribution for the total flow distribution, identical to the single-phase model, is observed, as expected. When olefin readsorption is significant, the behaviour changes for both the internal and external dynamics of the system. More than one α-value is observed for both the paraffin and olefin distributions internally and for the outlet flow.

PP-II-34

PHOTOCATALYTIC DISINFECTION OF *LEGIONELLA PNEUMOPHILA* ON Ag-DOPED TITANIA THIN FILM

Obuchi E.[a], Yanagi K.[a], Kato K.[a], Kuroiwa A.[b] and Nakano K.[a]

[a]Department of Chemical Engineering, Fukuoka University,
8-19-1 Nanakuma, Jonan-ku, Fukuoka 814-0180, JAPAN, eobuchi@fukuoka-u.ac.jp
[b]Department of Microbiology and Immunology, Fukuoka University School of Medicine, 7-45-1 Nanakuma, Jonan-ku, Fukuoka, 814-0180, JAPAN

Abstract

We investigated the photocatalytic disinfection of *Legionella pneumophila* (*L. pneumophila*) in water using titania thin film and Ag-doped titania thin film for comparison of their activities. Both photocatalytic thin films could disinfect *L. pneumophila* under UV irradiation, Ag-doped titania thin film have higher activity than un-doped one. Furthermore, Ag-doped titania thin film could slightly disinfect *L. pneumophila* without UV irradiation. As it has bactericidal effect even in the dark, it is possible to make up for a weak point of photocatalytic disinfection. We also observed scanning electron microscopy (SEM) Image of *L. pneumophila* after the photocatalytic disinfection. The cell wall of *L. pneumophila* was destroyed (dissolved) by Ag-titania thin film, and endotoxin, which is a kind of toxic contents in bacteria could decompose endotoxin below the detection limit.

INTRODUCTION

Legionella pneumophila (*L. pneumophila*) is well-known as a cause of serious pneumonia. In Japan, it is often detected in the facilities related to water such as hot-spring resorts and the cooling towers. In general, water is disinfected using chlorine. However, as bacteria have the tolerance against chlorine, they might become the cause of infection. Therefore, sterilization using photocatalyst attracts attention as a new sterilization method. In our previous paper [1], we have reported about new method to prepare the transparent titania thin film and it has the photocatalytic activity against organic compounds such as nitrophenol under UV irradiation. In this work, we investigated the photocatalytic disinfection of *L. pneumophila* in water using both titania thin film and Ag-doped titania thin film for comparison of their activity.

EXPERIMENTAL

Amorphous titania powder obtained as reported previously [1] was dissolved in hydrogen peroxide solution (30%, Wako Chemicals, Japan). When Ag-doped titania thin film prepared, silver acetate aqueous solution is added at the same time. Pre-cleaned quartz glass tube (id 10mm x od 12mm x length 270mm) was coated using titania or Ag-doped titania solution, dried at room temperature and calcined at 773K for 2 hours. Thus we could obtain titania or Ag-doped titania thin film inside the glass tube. 200ml of test solution included *L. pneumophila* was filled in the glass tube and circulated at a flow rate of 200ml/min. Black light lamps (6W x 4, wave length 300-400nm) located outside the glass tube was switched on to irradiate UV light, and then the sample was collected at intervals to estimate the presence of viable bacteria.

RESULTS AND DISCUSSION

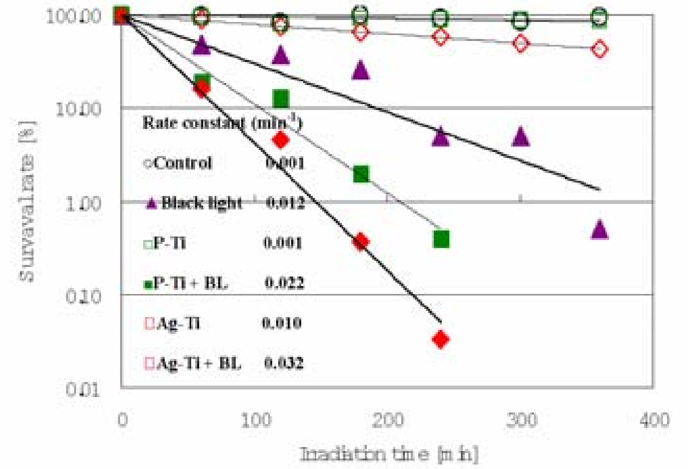


Fig. 1. Survival rate of *L. pneumophila* with process time.

Fig.1 shows the survival rate of *L. pneumophila* with process time on titania thin film (P-Ti) and Ag-doped titania thin film (Ag-Ti) under UV irradiation. The data follows a first order rate law, and the estimated rate constants (min^{-1}) shows in the figure. Without photocatalyst and no UV irradiation (Control) did not disinfect *L. pneumophila*. On the other hand, under UV irradiation, the survival rate of *L. pneumophila* decreased gradually without photocatalyst. In addition, in the case of using titania and Ag-doped titania thin films under UV irradiation, the survival rate of *L pneumophila* decreased rapidly. Surprisingly, Ag-doped titania could slightly disinfect *L. pneumophila* without UV irradiation. Fig. 2 shows the SEM images of *L. pneumophila* after the treatment for 24h. The cell wall of *L. pneumophila* was destroyed by Ag-titania thin film. Although the leakage of the endotoxin was detected, the endotoxin was photocatalytically decomposed after 24h of treatment.

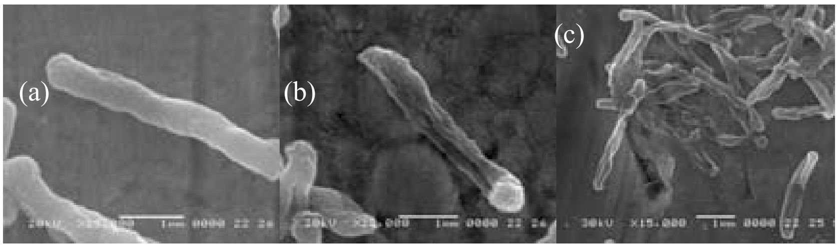


Fig. 2. SEM images of *Legionella pneumophila* treated with (a) control, (b) UV irradiation and (c) Ag-doped titania thin film under UV irradiation for 24h.

Reference

[1]. E. Obuchi et al., Kagaku Kogaku Ronbunshi (in Japanese) 21, 1075-1081 (1995).

TOWARDS INHERENTLY SAFER REACTOR DESIGN FOR COMPLEX REACTIONS

Pineda A.[1], Papadaki M.[2,3*], Saenz L.[1], Carreto-Vazquez V.H.[1],
Rogers W.J.[1] and Mannan M.S.[1]

[1]*Mary Kay O'Connor Process Safety Center, Artie McFerrin Department of Chemical Engineering, Texas A&M University, College Station, Texas 77843-3122, USA,*
e-mail: alba.pineda@che.tamu.edu; lina.saenz@chemail.tamu.edu; victor_carreto@neo.tamu.edu; wjrogers@tamu.edu; mannan@tamu.edu
[2]*IPSE, SPEME, University of Leeds, Leeds, LS2 9JT, UK,*
e-mail: m.papadaki@leeds.ac.uk.
[3*]*Corresponding author: Department of Environmental and Natural Resources Management, University of Ioannina, Seferi 2, Agrinio, GR 30100, Greece*
e-mail: mpapadak@cc.uoi.gr

1. INTRODUCTION

A number of reactive processes of the agrochemical, fine-chemicals and pharmaceutical industries involve thermally unstable and/or toxic reactants, products or intermediates, for which the chemistry, thermochemistry and thermodynamic properties are barely known. They frequently employ multipurpose batch or semi-batch reactors. In their current mostly empirical designs, these reactors are prone to runaways because: (a) the application of fine, sophisticated control is difficult due to the variety of productions served by the same reactor (b) due to their complexity, there is a complete lack or scarcity of kinetic and thermodynamic data [1]. Additionally, the impact on the environment of such, empirically designed batch-reactor processes, measured via the E-factor, namely the mass of by-products produced per unit mass of product, is very high and substantially higher than the respective ratio of other "traditional" large-scale, continuous, chemical processes [3].

This work addresses both the safety issues and the environmental implications that arise from the empirical design of added value chemicals production. It presents a methodology for the design of continuous, inherently safer and sustainable processes via the combination of calorimetry, computational chemistry, and reaction engineering.

The study focuses on small throughput added value processes that involve complex, homogeneously catalysed oxidations of organics, where hydrogen peroxide is the employed oxidant. In such reactors, hydrogen peroxide decomposition, producing gaseous oxygen is inevitable, while the organics present are often flammable. Hydrogen peroxide decomposition, which has been the cause of serious accidents, is condition dependent, for instance it is catalysed by traces of compounds such as metals, it is pH sensitive, and there is strong evidence that it is also autocatalytic [4-7].

The proposed design ensures operation at high synthesis reaction rates via operation at conditions where: (a) the synthesis reaction consumes most or all of the supplied hydrogen peroxide. (b) hydrogen peroxide accumulation in the reactor is constantly low, so that its accumulation in the reactor will not impose any threats in terms of safety, while the rate of its autocatalytic decomposition will be minimised (c) all the heat generated by exothermic reactions is utilised by the process, and (d) the reactor size is small, however, it is not a microreactor.

Case studies and preliminary experimental data will be shown.

References

[1]. Barton, J. A., & Nolan, P. F. (1989). Incidents in the chemical industry due to thermal-runaway chemical reactions. In IchemE symposium series no. 115, **1989**: 3–13.

[2]. Sheldom R.A., Catalysis and pollution prevention, Chem. Ind., 6 Jan **1997**:13.

[3]. Mackenzie, J., Considerations for the safe design of processes using hydrogen peroxide and organics. Plant/Operations Prog., **1991**. 10(3): 164-170.

[4]. Klais, O., Hydrogen Peroxide decomposition in the presence of organic material. A case study. Thermochim. Acta, **1993**. 225: 213-222.

[5]. Wehrum, W.L., Case Study of a Hydrogen Peroxide Related Deflagration in a Wastewater Treatment Tank. Process Saf. Prog, **1993**. 12(4): 199-202.

[6]. Lacoursiere, J.P., An explosion caused by mixing incompatible liquids. Process Saf. Prog., **2005.** 24(2): 115-119.

Acknowledgements

The financial support of this research by Mary Kay O'Connor Process Safety Center is greatly acknowledged.

INFLUENCE OF INTERNAL DIFFUSION ON CO PREFERENTIAL OXIDATION OVER Cu/CeO_{2-x} CATALYSTS

Potemkin D.I.[1,2], **Snytnikov P.V.**[1,2], **Sobyanin V.A.**[1,2]

[1]*Boreskov Institute of Catalysis SB RAS, Pr. Lavrentieva, 5,*
Novosibirsk, 630090, Russia
[2]*Novosibirsk State University, Pirogova St., 2, Novosibirsk, 630090, Russia*
potema@catalysis.ru

Preferential CO oxidation (CO PrOx) is a well known method for CO removal from hydrogen-rich gas mixtures. Wall coated catalytic microchannel reactors are favorable candidates for CO PrOx due to high heat and mass transfer rates achieved [1]. The present work aims at a systematic study of the preferential CO oxidation in hydrogen-rich gas mixtures over copper-cerium oxide catalyst in a microchannel reactor, in the presence of CO_2 and H_2O, to optimize washcoating procedure and reaction conditions to reach CO concentrations below 10 ppm.

Several series of copper-ceria catalysts for preferential CO oxidation were synthesized by various methods that allowed variation of the textural and morphological characteristics of the samples. The 5 wt.% copper catalyst prepared by impregnation showed the optimal catalytic performance and was deposited into the reactor's microchannels. The obtained samples demonstrated good impact-resistance, and survived contacts with water.

Catalytic performance of the washcoated catalyst in the microchannel reactor were checked using model feeds at WHSV = $50 \div 500$ L $g^{-1}h^{-1}$ and temperature $100 \div 300$°C (Fig.1).

It was observed that the reactions of CO and H_2 oxidation under wide range of reaction conditions proceeded independently using the same common reagent – O_2. This assumption helps to simplify the mathematical modeling and describe the observed kinetic dependencies by relatively simple equations. For both CO and H_2 oxidation reactions, power-law reaction rate equations were proposed to describe the reaction kinetics. The apparent activation energy of the both reactions and the reaction orders with respect to O_2 and CO have been determined.

Using the obtained rate expressions for CO and H_2 oxidation reactions, the effectiveness factors (η) for CO (Fig. 2) and H_2 oxidation reactions were calculated. The effectiveness factor for H_2 oxidation is equal to 1 in wide range of temperatures and coating thicknesses, because of the zero reaction order with respect to O_2. It can be seen that at temperatures higher than 200°C, the mass transfer limitation significantly influences the CO oxidation rate and appears to be one of the main factors that decrease the process selectivity.

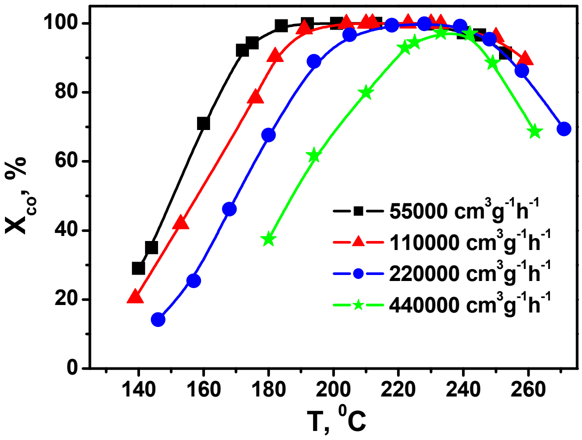


Figure 1. CO conversion as a function of temperature for different total flow rates. The reactant gas feed (vol. %): 1.5 CO, 1.6 O_2, 10 H_2O, 20 CO_2, 65 H_2 and He as a balance.

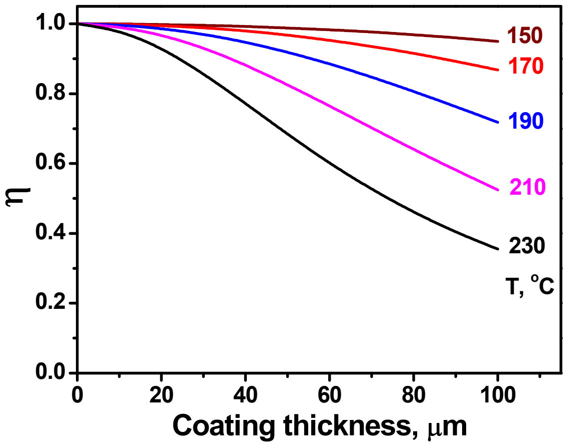


Figure 2. Estimated effectiveness factor for CO oxidation reaction at the entry point of reactor as a function of coating thickness for different temperatures. The reactant gas feed (vol. %): 1.5 CO, 1.6 O_2, 10 H_2O, 20 CO_2, 65 H_2 and He as a balance.

Mathematical modeling of the microchannel reactor operation was performed. Results of mathematical modeling were in good agreement with the experimental data.

References

[1]. Catal. Today **2007** 120 2-20.
[2]. Appl. Catal., A **2008** 350 53-62.

Acknowledgements

The work was partially supported by grants “UMNIK“ (FASIE), MK-5602.2010.3 (grants of Russian Federation President) and GC №185 of FFP “SSESIR 2009-2013”.

PP-II-37

ZEOLITES IN THE GAS PURIFICATION PROCESSES: INVESTIGATION AND SIMULATION

Prymyska S.[1], **Beznosyk Yu.**[1], **Reschetilowski W.**[2]

[1]*National Technical University of Ukraine (KPI), 03056 Kyiv, Ukraine,*
primiska@rambler.ru, prymyska@ukr.net
[2]*Institut für Technische Chemie, TU Dresden, 01062 Dresden, Germany,*
wladimir.reschetilowski@chemie.tu-dresden.de

INTRODUCTION

The harmful effects of nitrogen oxides on the environment have initiated intensive research for the design of efficient techniques for their abatement from stationary and mobiles sources. NO_x is the major atmospheric pollutant which is responsible for photochemical smog and acid precipitation problems. In contrast to the selective catalytic reduction of nitrogen oxides which is the good established method to reduce NO_x emissions, adsorption of NO_x is an alternative method which is especially effective for the concentrated removal of low concentrations of NO_x [1]. Adsorption of NO_x using zeolites has been an important research topic for the development of transport and stationary exhaust treatment systems [2]. In order to model the dynamics of the adsorption of nitrogen oxide on zeolites, the basic information required is the adsorption equilibrium isotherm of the pure components.

INVISTIGATION

Adsorption of NO_x has been experemantaly studied on various molecular sieves using the mass spectrometric method to determine the potential for separation of these common atmospheric contaminants from air. The molecular sieves studied include KA zeolite, 13X zeolite and LiLSX zeolite. The granular adsorbent (1.6-2.5 mm size; 35 g) was packed into the adsorber consisting of a vertical heatable glass tube. The adsorption and desorption experiments have been performed at varying temperatures and gas flow rates of 25, 30, …,50°C and 5, 10, 15 l/h, respectively. Equilibrium isotherm were produced in order to quantify sorbate capacity under various conditions. For the certain equipment, the main parameters (the gas flow rate, the weight of adsorbent, the temperature) were determined.

SIMULATION

In the isothermal adsorption systems the equilibrium relationship between the adsorbent and adsorbate can be characterized by single curve or isotherm, where the solid phase solute concentration is a function of the gaseous phase solute concentration characterized by the mass balance in the gas and solid phase [3]. A one-dimensional fixed bed model is derived from the mass balance in gas and solid phase [4], with the following assumptions: no temperature gradients and no concentration gradients in a bed section perpendicular to gas flow direction, the regime is isothermal; there is no deactivation of the adsorbent during the experiments.

$$\frac{dy_{out,i}}{dt} = \frac{2RT}{\varepsilon V_i P_t}\left[\frac{FP_t}{RT}(y_{in,i} - y_{out,i}) - k \cdot \overline{y_i} \cdot \theta_{V,i} \cdot q_0 \cdot w_i\right]$$

$$\theta_{V,i} = y_{in,i}\frac{dF}{dt}\frac{P_t M_{NO_x}}{RT}(t_s - \sum_0^{t_s}\frac{\overline{y_i}}{y_{in,i}}dt)$$

where F is the gas feed rate, y_{in}, y_{out} are the inlet and outlet mole fractions of adsorbate, P_t is the total pressure, R is the gas constant, T is the temperature, $\overline{y_i}$ is the average gas mole fraction in the i layer, V_i and w_i are the volume and the weight of the layer, ε is the void fraction, k is the rate constant, q_0 is the saturation amount of nitrogen oxide per unit weight of adsorbent.

For calculating the model of the adsorption process on agglomerated zeolite, the program package ZEOAD was developed. This program permits to calculate the changing of the initial concentration of nitrogen oxides depending on time. Also, one can get breakthrou curves under different specific parameters.

References

[1]. M.A. Go.mez-Garcı, V. Pitchon, A. Kiennemann Pollution by nitrogen oxides: an approach to NOx abatement by using sorbing catalytic materials // Environment International 31 (2005) pp. 445– 467.

[2]. John D. Sherman Synthetic zeolites and other microporous oxide molecular sieves Proc. Natl. Acad. Sci. USA Vol. 96, pp. 3471–3478, March 1999.

[3]. Statyukha G., Prymyska S., Beznosyk Yu., Reshetilowski W. Simulation the adsorption process of nitrogen oxides in zeolites. // 35rd International Conference of Slovak Society of Chemical Engineering, 26-30 may 2008, Tatranske Matliare, Slovakia. pp. 97 – 99.

[4]. Statyukha G, Prymyska S., Beznosyk Yu. Computer designing the adsorption process of nitrogen oxides in zeolite. // 18 th Intern. Congress of Chemical and Process Engineering, August 2008, Praha. – CHISA 2008.

PP-II-38

OPTIMIZATION OF LACTIC ACID-ETHANOL ESTERIFICATION BY 2^3 FACTORIAL DESIGN OF EXPERIMENTS

Rattanaphanee P.

School of Chemical Engineering, Suranaree Univeristy of Technology,
Nakhorn Ratchasima, Thailand, E-mail: panarat@sut.ac.th

Ethyl lactate is a monobasic ester formed during esterification of lactic acid with ethanol. Due to its low toxicity and inherently biodegradable, it is used commonly in food, cosmetic and pharmaceutical industries [1]. Apart from various application of the ester, esterification of lactic acid is currently a reaction widely investigated and employed in purification of lactic acid from its aqueous solution [2]. Establishing an optimal condition for this reaction is, therefore, a critical step that would lead to a highly efficient process for ethyl lactate formation. In this study, catalytic esterification of lactic acid with ethanol was carried out with an aim to deterimine the optimal conditions for the reaction using statistial experimental design approach. Influence of reaction parameters on conversion of lactic acid (Y) in this reaction was investigated. The parameters of interest included reaction temperature, (X_1: 65-85°C), initial reactant molar ratio ($X_2 = n_{ethanol}:n_{lactic}$: 1:1-5:1), and catalyst loading (X_3: 1-5 %w/v). All the experiments were performed at 300 rpm since effect of external mass transfer resistance was observed to be negligible at this degree of agitation.

Experimentally, conversion of lactic acid in esterification reaction was found to increase with individually increase of all parameters. Simultaneously increase of X_1 and X_2 as well as X_2 and X_3 also led to significantly elevating lactic acid conversion. However, raising X_1 and X_3 while keeping level of X_2 constant caused only slight increase of lactic acid conversion. A two-level, three-factor (2^3) factorial design of experiments [3] were applied to elucidate a relationship between these parameters. It was revealed that, in the range of parameters explored in this study, initial reactant molar ratio was the most significant parameter for the reaction conversion. A full model to predict conversion as function of reaction parameters was constructed from the experimental results and was found to be

$$\begin{aligned} Y &= 14.1773 + 0.3580X_1 - 3.4881X_2 + 7.9863X_3 + 0.1039X_1X_2 \\ &\quad - 0.1081X_1X_3 + 0.7923X_2X_3 - 0.0031X_1X_2X_3 \end{aligned}$$

As shown in Table 1, the calculated conversion was found to be in an excellent agreement with those obtained experimentally.

Table 1. Experimental and calculated conversion of lactic acid esterification in 2^3-factorial experiments.

Run	Temperature (°C)	Ethanol-Lactic Acid Molar Ratio ($mole_{EtOH}:mole_{LA}$)	Catalyst Loading %(w/v)	Coding			% Conversion of Lactic Acid	
				X_1	X_2	X_3	Experiment	Calculated
1	65	1:1	1	-1	-1	-1	42.261	42.261
2	85	1:1	1	+1	-1	-1	49.274	49.274
3	65	5:1	1	-1	+1	-1	57.674	57.674
4	85	5:1	1	+1	+1	-1	72.748	72.748
5	65	1:1	5	-1	-1	+1	48.467	48.465
6	85	1:1	5	+1	-1	+1	46.585	46.582
7	65	5:1	5	-1	+1	+1	73.333	73.331
8	85	5:1	5	+1	+1	+1	78.519	78.517

References

[1]. Zhang, Y., Ma, Li, Yang, J. Kinetics of esterification of lactic acid with ethanol catalyzed by cation-exchange resins. *React. Funct. Polym*. **2004**. 61: 101-114.

[2]. Kumar, R., Mahajani, S.M. Esterification of lactic acid with n-butanol by reactive distillation. *Ind. Eng. Chem. Res*. **2007**, 46, 6873-6882.

[3]. Mongomery, D.C. Design and analysis of experiments. 6th ed. USA, John Wiley & Son, **2005**, 265-280.

Acknowledgements

The financial support for this work is from PTT Plc. Thailand. The author is also greatful to Mr. Peetikamol Kongsamai and Ms. Boonpradab Daengpradab for their help in the experiments.

PP-II-39

POLYMERIZATION REACTOR FOR THE EVALUATION OF CATALYSTS TYPE HONEYCOMB

Rebollar B.M., **Silva E.Y.**

Instituto de Investigaciones y Desarrollo Industrial SC, Oriente 101 3605,
Col Río Blanco, 07850 DF MEXICO, mrebollar@inidi.org

There are great variety of laboratory reactors for catalysts evaluation [1,2], but in the case of polymerization, the complications are avoided and almost all reactions are realized are on homogeneous form. The selection of the form of the catalyst to using in a reaction is an important stage in the design of the reactor and in the laboratory must be the first step, normally spheres or pellets are used, but in case of polymerization to use this type of catalysts not always is a good idea, because during some polymerization reactions the viscosity varies in to large range and the level of liquid is not constant. If mixing is not well affected at all reactor, and at every point in the catalyst the reaction presents a low yield, due to hot spots, dead zones and a low or even any molecular diffusion, for it the polymers industry continues using the homogeneous reactions, assuring this way the close contact between the catalyst and the reactants. To use honeycomb monolith as catalysts in the polymerization allows a laminate flow, achieving this way a close contact with the catalyst.

The designed reactor allows the evaluation of honeycomb monoliths, is of glass with a capacity of 300 ml, the catalyst is of 1.8 x 1.8 x 0.4 cm, of square channels of 1.2 mm. It can be used of constant form or for lots.

The reactor was tested in the reaction of amination of the polydimethylsilxane, reaction of 24 hours for concluding [3], the catalyst was alúmina, impregnated by washcoat with platinum, to evaluate the conversion of the reaction it was used infrared spectroscopy, the system was compared with the same reaction in the same time in a homogeneous phase.

The reactor was evaluated in the following concepts; Sampling and analysis of product composition, isothermality, residence-contact time measurement, selectivity time averaging disguise, molecular diffusion of the reactants in the catalyst determining the effectiveness factor, construction difficulty and cost.

The molecular diffusion was evaluated by means of the system proposed by Hayes [4] and the obtained results show that the kinetic of the reaction is not limited by its molecular diffusion, as it is confirmed by the resultant conversions that are better to the obtained in the homogeneous system. With the rest of the evaluated concepts the reactor shows superior qualifications to other laboratory reactors of major complexity and cost, so it is confirmed the possibility of being able to use this reactor in the evaluation of catalysts on polymerizations reactions.

References

[1]. Carberry J.J., Ind Eng Chem, **1964,** 56, 39-46.
[2]. Forni L., Catal. Today, **1997**, 34, 353-367.
[3]. Ryan J.W., Speier J.L., J Org. Chem., **1966**, 31, 2968-2974.
[4]. Hayes R.E., et al, Appl Catal., B, **2000**, 25, 93-104.

TWO-ROTOR APPARATUS

Reznichenko S.O., Ratasep M.A., Verigin A.N., Kukushkin M.S., Lebedev S.N.

Saint-Petersburg State Institute of Technology (Technical University),
St. Petersburg, Russia, cbeta.p@mail.ru

The MAHP department of St. Petersburg Institute of Technology has developed a highly efficient rotary apparatus with a multifactorial impact on working area. Interaction between the phases occurs in vigorous stirring gas-liquid layer with well-developed and rapidly updated interfacial surface under the field of centrifugal forces, along with a compulsory fluid flow from one stage to another.

The apparatus consists of two rotors. The rotor consists of a thin shaft with a set of perforated disks fixed on it. The rotors are located in the "8" shaped cross section body so, that the disks fixed on one rotor rotating between the disks of the other one.

Rotors provide a discrete input of mass and energy of high density into the working area. Perforation allows the gas bubble through the liquid. The acoustic oscillations produced by the rotors dramatically speed up the heat&mass transfer at frequencies close to the natural oscillations.

The apparatus can operate in a continuous or periodic mode. In continuous mode, phases are fed countercurrently. The device has a low hydraulic resistance and can operate over a wide range of loads on the liquid and gas.

Hydraulic resistance of the apparatus can be calculated on the basis of two-stream model, whereby the gas flow through the apparatus, can be regarded as consisting of two independent parts: the flow going straight up through the perforated disk and flow going along the zigzag channel.

Hydraulic resistance of moistened disk can be regarded as one of the dry disk, but with reduced porosity, depending on wetting conditions.

Experimentally it was shown that mass transfer in the apparatus can be well described by the volumetric mass transfer coefficient k_{Vx}:

$$k_{Vx} = c\left(\varepsilon_V \frac{h_{eff}}{h} \right)^n ,$$

where h_{eff} – effective gas-liquid layer height; h – contact stage height; ε_V – energy dissipation rate; c, n - constants.

Hydrodynamic regime in the apparatus for large values of Re are very similar to the grid-generated turbulence. Such structures are well described by Kolmogorov's hypothesis of local isotropy [1], on the basis of which we had obtained the following dependence

$$\varepsilon_V = \left(1 - \Phi\left(\frac{\mathrm{Re}^* - \mathrm{Re}_{tr}}{\frac{\sqrt{2}}{3}\mathrm{Re}_{tr}}\right)\right) \cdot A \cdot \mathrm{Re}^{*2} + \Phi\left(\frac{\mathrm{Re}^* - \mathrm{Re}_{tr}}{\frac{\sqrt{2}}{3}\mathrm{Re}_{tr}}\right) \cdot \gamma \cdot \mathrm{Re}^{*3},$$

where **Re*** – modified Reynolds numbe**r**; **Re*tr*** – transition Reynolds number; **Φ** – cumulative distribution function; *A*, γ – constants.

Centrifugal Reynolds number contain a geometric complex, corresponding to the squared characteristic linear dimension, this complex can be conveniently represented as the product of stage height *h* in power α and diameter *D* in power β. The sum of α and β must equal 2, or $\beta = 2 - \alpha$. Since that hydrodynamic and geometrical similarity could be determinate with following numbers

$$\mathrm{Re}^* = \mathrm{Re}\,\Gamma \qquad \mathrm{Re} = \frac{nD^2}{\nu} \qquad \Gamma = \left(\frac{h}{D}\right)^{\alpha}$$

Based on our models we designed an apparatus for urea reduction of NOx process unit in Angarsk Catalysts and Organic Synthesis Plant [2].

$$3\ \mathrm{CO(NH_2)_2} + 3\ \mathrm{NO} + 3\ \mathrm{NO_2} \longrightarrow 3\ \mathrm{CO_2} + 6\ \mathrm{N_2} + 6\ \mathrm{H_2O}$$

The process unit successfully cleaned the gas up to the sanitary norms. The experiments have confirmed the adequacy of the developed models and the apparatus high efficiency.

The apparatus can be used in many processes: it can work as absorber, rectifying column or reactor.

References

[1]. Verigin A.N., Ignatyev M.A. (**2003**) 'Stirring fluids at high energy dissipation rate'. Int. Ecology Energy Economics VII, pp. 166-176 (in Russian).

[2]. Reznichenko S.O., Ignatyev M.A. (**2008**) “Urea reduction of NOx”, Int. Young Scientists to North-West Region Industry, p.92 (in Russian).

The authors wish to express their gratitude to Mrs. Tselyutina M.I., the deputy chief of the Research and Control Center – the chief of the scientific research development of the Angarsk Catalysts and Organic Synthesis Plant, without whose knowledge and assistance this study would not have been successful.

PP-II-41

TECHNICAL ECONOMICAL OPTIMIZATION OF INDUSTRIAL REFORMING REACTOR BY MATHEMATICAL MODELLING

Sharova E.S.[1], Klimova E.S.[1], Karakulov A.G.[2], Ivanchina E.D.[1]

[1]*Tomsk Polytechnic University, Tomsk, Russia, e-mail: sharova@sibmail.com*
[2]*"Achinsk refinery East Oil Company", Achinsk, Russia*

The catalytic reforming process is the main part of high-octane petrol production. Resource management of the production mainly depends on the catalyst. A mathematical model based on physicochemical principles allows trying different platinum contacts for finding an optimal catalyst and producing motor fuel of better quality and in greater quantities. The modeling system built on this model provides the calculation of the optimal apparatus reconstruction and technological conditions of its work. This increases the life of the platinum contact.

Mathematical modelling of the reaction apparatus is a multistep process that begins with an examination of the laws of chemical reactions with subsequent kinetic description. Then it is to solve the inverse kinetic problem and to establish the adequacy of the mathematical model to the real process. The last step is to create the intellectual system for predicting the catalyst activity and process integrated circuits with the estimation of technological, economic and environmental criteria. Taking into account the catalyst efficiency, the mathematical model of the device is described by the following system of differential equations:

$$\begin{cases} G_f \dfrac{\partial C_i}{\partial Z} + G_f \dfrac{\partial C_i}{\partial V} = \sum\limits_j W_j \cdot \eta_j \\ G_f \dfrac{\partial T}{\partial Z} + G_f \dfrac{\partial T}{\partial V} = -\dfrac{1}{C_p^{mix}} \sum\limits_j \Delta H_j \cdot W_j \cdot \eta_j \end{cases}$$

$$Z = 0 \quad T = 0 \quad C_i = 0;$$
$$V = 0 \quad T = T_0 \quad C_i = C_{i,0};$$

where Z – the total amount of recycled raw materials, m^3; V – catalyst volume in a reactor, m^3; G_f – flow of product mixture, m^3/h; C_i – concentration of the i-th component at the reactor inlet, mol/m^3; W_j – the j-th reaction rate, $mol/(m^3 \cdot h)$; η – the extent of the inner surface of the catalyst grain (efficiency factor).

The investigations showed that the objective criterion at the process optimization and evaluation of economic efficiency is the degree of the catalyst potential usage. It is numerically equal to the deviation of the current activity from the optimum. The optimal activity provides a balance of formation and hydrogenation reactions of intermediate products and increases the duration of the catalyst work.

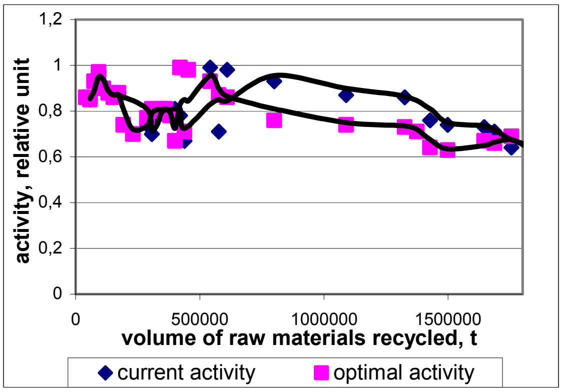


Fig. 1. Dependence of the catalyst R-98 activity on volume of recycled raw materials

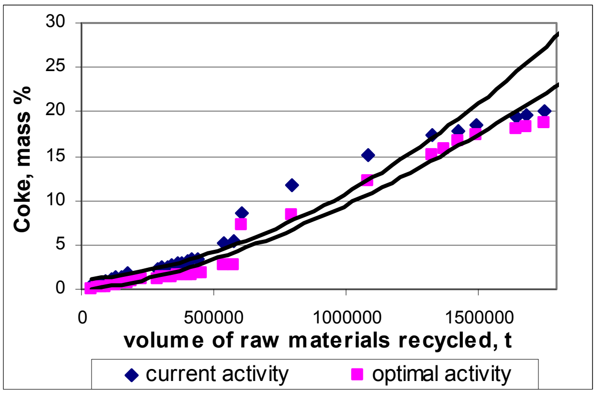


Fig. 2. The coke accumulation on the catalyst R-98

Our researches were carried out on the reforming unit with a fixed-bed of catalyst. The results showed that during the studied period the value of the current activity was higher than optimal (Fig. 1). This led to the increasing of coke accumulation – up to 20 mass % by the end of the cycle. But it would be less (18.25 %) if the current activity was equal to the optimal activity at a given octane number (Fig. 2).

The product yield is higher by 2.18 % when the catalyst works at optimal activity. Taking into account that in Russia 1 ton of gasoline with octane number 92 costs 335.5 dollars the average lost profits of companies working at current activity is an average of 2.69 million dollars per year (Table 1).

Table 1. The lost profit of a company working at current activity

Raw materials recycled, mln. ton	**Product yield, mass %**		**Loss of raw material, mass %**	**Loss, mln. dollars/year**
	Current activity	**Optimal activity**		
0.04	82.96	86.53	3.57	0.48
0.07	84.36	87.27	2.91	0.68
0.09	85.69	87.29	1.60	0.48
0.13	84.47	87.10	2.63	1.15
0.17	85.35	87.90	2.55	1.45
0.33	85.84	88.51	2.67	2.96
0.42	85.88	87.94	2.06	2.90
0.61	83.69	87.67	3.98	8.15
1.09	85.54	86.74	1.20	4.39
2.16	86.57	87.86	1.29	9.35
Average	**85.18**	**87.36**	**2.18**	**2.69**

Thus, application of the software mathematical model based on physicochemical principles makes it possible to optimize the reactor work and reduce production cost.

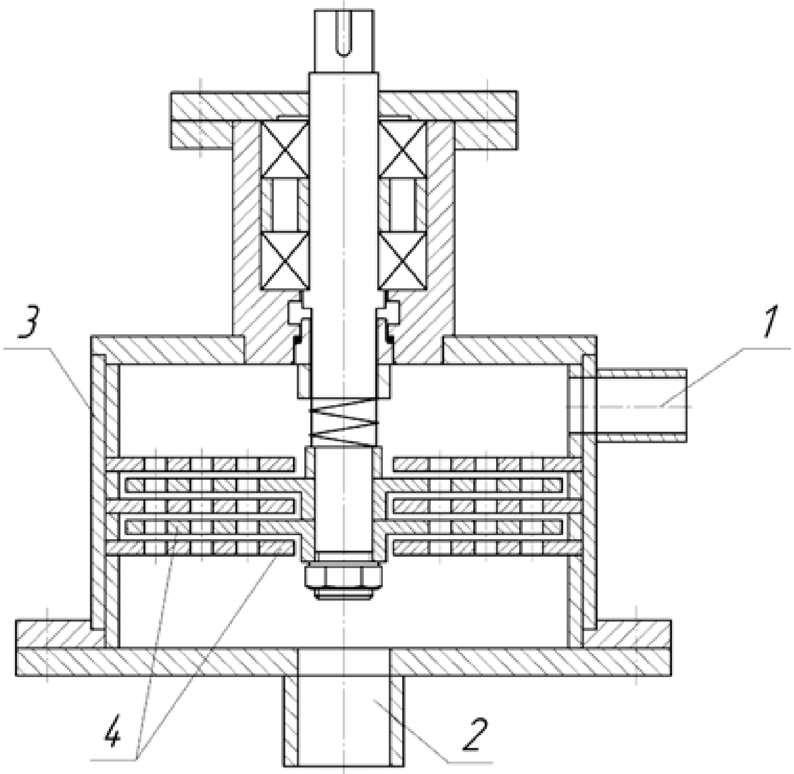
PP-II-42

MICRO REACTORS ON THE PLATFORM OF ROTOR-DISK MIXERS

Shulayev N.S., Nikolaev Y.A.

Ufa State Petroleum Technological University, Ufa, Russia

In order to increase effectiveness of carrying out of heat and mass exchange processes, there are new reactionary devices and apparatus are being developed, and existing apparatus are being improved. Small rotor-disk mixers [1] could be singled out among perspective dynamic apparatus that meet the energy saving requirements, compact in size and have desired productivity. Such devices are devices with cylindrical case which contains two groups of operable elements in the form of smooth or corrugated disks – rotating rotor and static stator with perforation (drawing 1).



1 – Input branch pipe, 2 - Output branch pipe,
3 – Static cylindrical case, 4 – Perforated disks
Drawing 1 – Schematic option of the rotor-disk mixer

Devices of this type provide significant increase in surface separation of mixed components during processing of liquids. These devices successfully being used as effective micro reactors in carrying out chemical transformations in heterogeneous environments: liquid-liquid, liquid-gas and liquid-solid disperse particles [2, 3, 4].

One of the major indicators of efficiency of carrying out heat-mass exchange processes in such rotor-disk mixers is the size power dissipation. This indicator in this case most fully corresponds to quantitative characteristics of process and defines changes of properties of the processed environment.

Power, dissipated at all steps of the rotor-disk micro reactor (step is one rotating and one stationary perforated disk) could be defined precisely enough for laminar modes of processing of a mix under the formula (1).

$$N = \sum_{i=1}^{k} \frac{\pi\mu \mathrm{Re}_{zi}}{4h_i} \cdot \frac{\omega^2 (R_{Д}^4 - R_B^4)}{(1 - e^{-\mathrm{Re}_{zi}})} \;, \qquad (1)$$

where $$\mathrm{Re}_{zi} = \frac{v_{zi}\rho h_i}{\mu}, \; v_{zi} = \frac{G}{\rho n_i S_{отвi}},$$

i - number of steps (gaps) between stationary and rotating disks, $1 \le i \le k$;
μ - dynamic coefficients of viscosity, Pa·s.
ρ - mix density, kg /m^3;
G - mass consumption of a processed mix, kg /s;
ω - angular speed of a shaft, s^{-1};
$R_Д$ - disk radius, m;
R_B - shaft radius, m;
h_i - gap between disks i steps, m;
n_i - number of apertures i disk;
$S_{отвi}$ - aperture area i disk, m^2.

References

[1]. Shulayev N.S., Nikolaev Y.A., Ivanov S.P. Small rotor-disk mixers. // M.: Chemistry, 2009. – 186 p.

[2]. Shulayev N.S., Nikolaev Y.A., Boev Y.V., Shiriyazdanov R.R., Afanasenko V.G. Clarification of drains of manufacture hypochlorite calcium in rotor the dezintegratore-mixer / Ecology and the industry of Russia. – 2008. - № 2. - P. 6-7.

[3]. Shulayev N.S., Nikolaev Y.A., Boev Y.V., Ivanov S.P. Rotor the dezintegratore-mixer for carrying out gas-liquid reactions to an example carbonization a soda solution / Chemical technology. – 2008. - № 4. - P. 173-176.

[4]. Shulayev N.S., Nikolaev Y.A., Shiriyazdanov R.R. Mixer for removal of by-products from dichlorethane in manufacture vinyl chloride / Oil refining and petrochemistry. - 2008. - № 3. – P. 52-54.

PP-II-43

THE AUTOTHERMAL REACTOR OF NATURAL GAS CONVERSION TO SYNTHESIS GAS ON BASIS OF BLOCK SHS CATALYST

Sidorova O.I., **Galanov S.I.**

Tomsk State University, 36, Lenin Ave., Tomsk, Russia
E-mail: galanov@xf.tsu.ru

The partial catalytic oxidation of natural and oil gases at short times of contact on block catalyst is perspective process for receipt of synthesis gas in compact reactors. The autothermal reactor of receipt of synthesis gas with productivity to 10-15 m^3 synthesis gas in 1 hour was developed (figure a).

As catalysts use porous disk and cylinder by means the method of self-propagating high-temperature synthesis (SHS), which is compound metal-ceramic with composition: *Ni – 52.9,* Al_2O_3 *– 5.0, MgO – 17.2,* $MgAl_2O_4$ *– 14.9,* ZrO_2 *– 9.5, CaO – 0.5 % mass.*

The autothermal reactor: 1- chamber of air and natural gas mixture, 2- fire-resistant SHS plate, 3- catalytic block, 4- outward heat exchanger.

The start of reactor: the mixture of natural gas and air in ratio 1/8-9 (vol.) give to reactor, heat up keep-alive spiral, methane take fire and heat up of catalytic block. The temperature control conduct of thermocouples, which situated in block. At temperature about 500-600 °C reactor moved in conditions of synthesis gas generation.

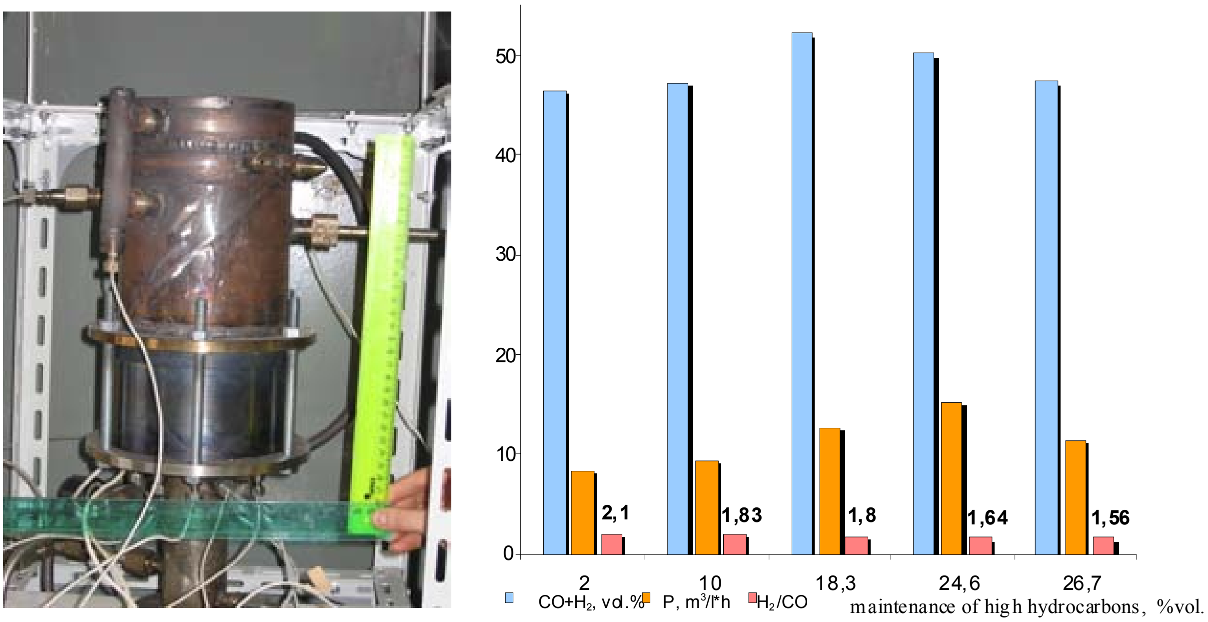
The conditions of synthesis gas generation**:** the ration of natural gas and air is 1/(2.4-2.9) (vol.). The temperatures (depend on velocity gas stream, ration, heating of air, pressure): exit from fire-resistant SHS plate - 190–360 °C; entry of catalyst – 830-1040 °C; middle of catalyst – 870–250 °C; exit from catalyst - 680–870 °C; temperature of heat exchanger - 480–750 °C; temperature of incoming air – 25–455 °C. The heat exchanger get hot not only of synthesis gas, but and of catalyst radiant stream. The temperature of synthesis gas after catalytic block is 300-450 °C. After condensation of water reaction gases to have composition: H_2 – 30-34 %; CO – 15-18 %; CO_2 – 2 -3 %; CH_4 – 0,5 -4 %, everything else N_2 (% vol.). The quantity of produce water to correspond quantity of CO_2: on 1 kg CO_2 form 0,8 kg water. The pressure can change from 1 to 4 atm. The increase of pressure leads to evening-out of temperature gradient and raises of synthesis gas yield on 2-5 %. The accessory addition of water vapor not leads to the increase of synthesis gas yield.

These conditions are conformably to mixture of natural gas: methane 98-95 % vol., everything else ethane, propane, butane, nitrogen, CO_2.

The ration carbon/oxygen changes from 0,63 to 0,75 kg/kg at use of natural gas with contents of propane and butane to 25 % vol.

The ration of high hydrocarbons C_{2+} to methane changes from 2,0 to 24,6 % vol. The temperature in catalyst changes from 850 to 1250 °C depends to mass expense of mixture. The productivity on synthesis gas is 8-20 m^3/l catalyst in 1 hour at conditions of exploitation of catalytic block.

The concentration of carbohydrates C_{2+} in gas for conversion can amount to 24–26 % vol. (figure. b) without change in work of catalyst. For conservation of temperature procedure and high yield of synthesis gas it is necessary exactly back up the ration of carbon (kg)/oxygen (kg) = 0,72-0,75.



a. ***b.***

Figure. a) Outward appearance of autothermal reactor; b) The influence of maintenance of high hydrocarbons in natural gas on concentration $CO+H_2$, ration H_2/CO and productivity on synthesis gas(P, m^3/l·h)

The addition of water vapor in natural gas (with predominance of methane – 98 % vol.) not leads to the change of synthesis gas yield. In case of use gas with maintenance of high hydrocarbons C_{2+} about 24 % vol. the increase of pressure and presence of water vapor in system leads to increase of synthesis gas yield to 51–52 % vol. at ration H_2/CO ~ 2.

This work was supported by the Russian Federal Program "Scientific and scientific-educational professional community of innovated Russia".

NONISOTHERMAL MATHEMATICAL MODELS FOR FISCHER – TROPSCH PROCESS IN THREE – PHASE FLUIDIZED BED ACCOUNTING FOR GAS DISSOLVED COMPONENTS CONCENTRATIONS CHANGE IN SUSPENTION DURING THE REACTION. THE PROFIT OF PRELIMINARY INERT LIQUID PRESATURATION BY SYNTHESIS – GAS AND USE THE SPATIAL PACKING FOR GAS – LIQUID FLOW HYDRODYNAMICS IMPROVEMENT

Zhukova Olga[1], Stefoglo Evgeny[2]

[1]*Siberian State Technology University, Krasnoyarsk, Russia, zhukovolga@yandex.ru,*
[2]*ALCAR Chemical Group, Versher, Canada, stefevg@aol.com*

In the last Reports concerning methanol synthesis in slurry bubble column reactor (SBCR) with an inherently high heat removal capability.

This is a new concept to couple SBCR installation with coal-based integrated gasification combined cycle (IGCC) facility to co produce electric power and methanol. Methanol produced by coal-based IGCC operations should be lower cost than methanol produced by conventional methanol - only units, and cold displace higher priced methanol from other sources. In such kind of reactors high ratio CO/H_2 can utilize which are produced by new syngas generators.

Advances in kinetics studies are going on, and improvements in established laboratory kinetics models and expansion in the mechanism searching space are stressed. Considerable data have been obtained both in experimental and theoretical fields. A key aspect of an F-T catalyst is that it must promote CO activation.

Two columns were utilized for hydrodynamic studying 10 and 20 of diameter and 2 lengths. Special packing proposed of 2% specific volume and isotropic characteristic. Industrial powder catalyst, glass balls and sound as solid phase were used. Gas and solid phases hold up were measured in bubble column, three-phase fluidized bed with and without packing. By tracer technique axial dispersion is determined. It was found considerable effect by using packing, especially at high gas flow rate. The equations were found for solid hold up and Pe in liquid are proposed. For studying initial condition in gas - liquid processes on solid suspended catalyst 1 liter volume batch in liquid reactor were used. Commercial processes of catalytic hydrogenation on Pd/C powder catalyst at the range of temperatures 20-250 °C and pressures 1-40 bar were studied. Stirrer speed and gas flow rate also changed.

For the hepten, alpha-methylstyren and ether of paranitrobenzoic acid hydrogenation (anesthesin production) at the range of 20-80 °C and 1- 6 bars on Pd/C (40 microns of particular diameter) by using special technique the hydrogen dissolved concentrations during the reaction runs in suspension were measured. In the case when initial solution to be hydrogenated was by gas presaturated the conversion of the reaction is higher.

A mathematical model proposed which accounting for of influence of initial condition on the performance of the different types of gas-liquid reactors: the preliminary saturation of a reaction solution before the reactor (continuous or before the reactor (batch) in comparison with “usual” mode of operation. Such kind approach was successfully used for Loop - Ventury reactors investigations.

At the Fischer - Tropsch synthesis inert liquid also can be presaturated by syngas before the reaction zone. Here we propose non isothermal, non stationary model accounting for different way of hydrogen and carbon oxide dissolution when the temperature is change. Plug flow in gas phase, axial dispersion on liquid and temperature along axis are considered. Solid phase distribution is describing by diffusion model. Two initial conditions are accepted: liquid is saturated by gas and another case – “usual” mode of operation. For models calculation liquid Pe number values, mass transfer data and phases hold up have been taken for the case of fluidized bed with packing.

Many examples have been made by analyzing of model equations by different temperatures, catalyst loading gas and liquid flow rates. Accounting for gas solubility increasing both for hydrogen and carbon oxide with temperature increasing it seems that adiabatic regime will be favorable. According catalyst distribution along the height of column at the bottom concentration of catalyst is elevated and syngas dissolved level is also high, then rate of the reaction and consequently heat generation is also considerable. At the top of the reactor catalyst concentration is low and due to syngas consumption its (H_2+CO) concentration is also small.

Utilizing of packing and inert liquid medium by gas presaturation does the possibility to decreasing the reactor length, high syngas conversion by one path.

OPTIMIZATION METHODS FOR A SEQUENCE OF EXHAUST GAS CONVERTERS

Štěpánek J.[1], Kočí P.[1], Kubíček M.[2], Plát F.[1], Marek M.[1]

[1]Dept. of Chemical Engineering, [2]Dept. of Mathematics, Institute of Chemical Technology, Prague. E-mail: jan.stepanek@vscht.cz

The exhaust gas emission limits of internal combustion engines (used widely in transportation and power generation) are continuously being tightened. Particularly for lean-burn engines the exhaust gases need to be treated by a catalytic system (consisting of various monolithic reactor types, e.g. oxidation catalyst, NOx storage and reduction converter, and converter for selective catalytic reduction) [1, 2].

The mathematical model of a catalytic converter is formed by a system of partial differential equations describing mass and enthalpy balances including mass and heat transport and reaction rate expressions. The partial differential equations are solved by a finite difference method with (semi-)implicit difference approximation [3]. This paper describes the use methods of mathematical optimization to find optimal parameters of each reactor in a cascade with respect to individual components conversions (CO, HC, NOx) while considering given restrictions (e.g., total system volume, maximum emissions allowed). The solution of this multi-criterional problem leads to Pareto sets. Pareto sets are such sets of solutions, where (in order to maintain optimality) one criterion must be sacrificed when another one improves. Pontryagin's maximum principle may be used for finding the optimal operation conditions, e.g. minimization of additive consumption for selective catalytic reduction of NOx while maintaining high NOx conversion.

References

[1]. Güthenke A., Chatterjee D., Weibel M., Krutzsch B., Kočí P., Marek M., Nova I., Tronconi E. Current status of modeling lean exhaust gas aftertreatment catalysts. *Adv. Chem. Eng.* **2007**, 33, 103-211.

[2]. Schejbal M., Marek M., Kubíček M., Kočí P. Modelling of diesel filters for particulates removal.*Chem. Eng. J.* **2009**, 154, 219-230.

[3]. Štěpánek J., Kočí P., Plát F., Kubíček M., Marek M. Investigation of combined DOC and NSRC diesel car exhaust catalysts. *Comp. Chem. Eng.* **2010**, In press, doi:10.1016/j.compchemeng.2010.01.003.

Acknowledgements

This work has been supported by the Czech ministry of education (Project MSM6046137306), the Czech grant agency (project 104/08/H055 and 104/08/1162) and the Institute of Chemical Technology, Prague.

PARTIAL OXIDATION OF METHANE INTO HIGHER HYDROCARBONS IN PLASMA-CATALYST COMBINED SYSTEM

Dong Jin Suh, **Jae-Wook Choi, Young-Woong Suh**

Clean Energy Center, Korea Institute of Science & Technology,
Cheongryang, Seoul 136-791, Korea, djsuh@kist.re.kr

Due to the depletion of oil and rise of oil price, the need for alternative chemical feedstock will be increasing in the near future. Methane, which is the principal component of most natural gas reserves, is the cheapest and abundant source for hydrocarbons. Methane can be indirectly converted to liquid fuels or other chemicals by way of synthesis gas, or directly transformed to C2 hydrocarbon or methanol. The oxidative coupling of methane is one of promsing route for direct methane conversion [1,2]. The intensive studies have been carred out to develop new catalysts with higher activity and selectivity for oxidative coupling of methane. However, efficient catalyst has not been found yet. So, many studies on the methane conversion using plasma processes are being performed as an alternative tool [3-5]. In plasma processes, methane can be easily activated by energetic electrons. But it was very difficult to control the reaction pathway to obtain the desired products under plasma state. In this work, we utilized catalysts to enhance the activity and selectivity for oxidative coupling of methane. The performance of plasma-catalyst combined system was evaluated in terms of conversion and selectivities.

The dielectric barrier discharge was chosen as a plasma source due to easy control of plasma generation and low power consumption. Preliminary experiments using plasma without catalyst were carried out at the fixed applied voltage of 3 kV to find the optimum experimental conditions. The methane to oxygen ratio was in the range of 4-8 and the total flow rate was fixed at 33 ml/min. The plasma zone was varied from 5 to 20 cm. The main products of converted methane were C2-C4 hydrocarbons, carbon dioxide and synthesis gas (H_2 and CO). Experimental results showed that metane conversion and hydrocarbon yields were increased with methane to oxygen ratio and plasma zone. The highest C2 yield was about 12.5% at the methane to oxygen ratio of 8 and the plasma zone of 20 cm. From these results, additional experiments using plasma with catalysts were conducted under the same conditions. MgO, CeO_2/MgO, La_2O_3/MgO, $BaCl_2$/Nd_2O_3, Zeolite Y, FER, and MOR catalysts were employed in the bottom of plasma zone. The amount of catalysts packed inside the reactor was 0.2 g. Table 1 summarized the effect of various catalysts on methane conversion and selelectivities. As catalyst was introduced into plasma zone, methane conversion was decreased from 36.4 % to 31.2-35.4 % according to catalysts whereas the selectivity of C2 and C2-C4 were increased by 3-6 % and 8-16 % respectively. As a result, C2 yield did not show any noticeable changes and C2-C4 yield was slightly increased by 1-4 %. The highest yield of C2 and C2-C4 was 13.3 % and 25.6 %, respectively in case of 1 wt % La_2O_3/MgO catalyst. The selectivity of CO and CO_2 was decreased with catalyst.

From the above results, the introduction of catalysts into plasma zone could be helpful to enhance product selectivity and to inhibit the unwanted oxdiation products such as CO and CO_2. Now further study is necessary to elucidate the role of catalyst under plasma state.

Table 1. The effect of catalysts on methane conversion and selectivities.

Catalyst	Conv. (%)	Selectivity (%)				C2 Yield (%)	C2-C4 Yield (%)
	CH_4	CO	CO_2	C2	C2-C4		
Blank	36.4	7.1	3.4	34.4	60.5	12.5	22.0
MgO	32.4	4.6	2.5	39.8	70.6	12.9	22.8
1 wt% CeO_2/MgO	32.5	3.4	1.9	39.3	71.0	12.8	23.0
1 wt% La_2O_3/MgO	35.4	6.3	3.1	37.6	72.4	13.3	25.6
zeolite Y	31.7	5.0	3.3	40.1	72.2	12.7	22.9
FER	31.3	2.8	1.6	40.9	76.0	12.8	23.8
MOR	31.2	4.5	1.9	39.8	72.0	12.4	22.5
15 mol% $BaCl_2$/Nd_2O_3	31.4	2.8	1.5	39.1	68.2	12.3	21.4

References

[1]. J. A. Sofranko et al., *J. Catal.*103 (**1987)** 302.

[2]. H. S. Zhang et al. *J. Catal.*112 **(1988)** 366.

[3]. S. L. Yao et al., *Energy & Fuels* 14 **(2000)** 910.

[4]. C. J. Liu et al., *Plasma Chemistry Plasma Processing* 21 **(2001)** 301.

[5]. M. Heintze and M. Magureanu, *J. Catal.* 206 **(2002)** 91.

Acknowledgements

The authors would like to acknowledge funding from the Korea Ministry of Knowledge and Economy through “Project of next-generation novel technology development” of KEIT.

DEVELOPMENT OF VORTEX APPARATUSES/DEVICES FOR THE PROCESSES INVOLVING GAS, LIQUID AND SOLID PHASES

Trachuk A.V.[1], **Kuvshinov G.G.**[2]

[1]*Boreskov Institute of Catalysis SB RAS, Prosp. Akad. Lavrentieva, 5,*
Novosibirsk 630090, Russia, e-mail: trachuk@ngs.ru
[2]*Novosibirsk State Technical University, Novosibirsk, Russia, e-mail: tpanstu@ngs.ru*

One method to enhance heat-mass exchange processes accompanying gas, liquid and solid phase interactions is to provide their contact in a centrifugal force field. Rotation results in the appearance of centrifugal forces in the multiphase layer, which results in large phase contact surfaces and relative phase rotation rates. A centrifugal force field can be generated by flux whirling. In the literature, the devices relying on this principle are known as vortex devices.

We suggest that for the vortex devices with a multiphase layer/bed, one can use the mathematical models developed for the multiphase systems in the gravitational field by replacing the value of gravity acceleration with a centrifugal one. To use this idea/suggestion, it is necessary to know the value of rotational rate of a multiphase layer regarding the geometry of a vortex apparatus, rates of gas and liquid flows and physical features of the phases.

Thus, for the suspended/slurry gas-liquid-solid layer (see Fig. 1a), containing small particles (<0.3 mm) at a volume concentration of solid particles reaching 25% in the liquid, one can consider a mixture of particles and the liquid phase as a homogeneous liquid possessing the effective density of a suspension. Pressure drop/differential and rotation rates in vortex apparatuses can be calculated by the known equations for the gas-liquid layer, in which effective density of a suspension is used instead of density of a liquid.

Fig. 1. a) Gas-liquid vortex layer; b) a three-phase vortex layer

On the procession of experimental data on the three-phase granular layer (Fig. 1b), we suggested that the gas-liquid emulsion filtrated through the granular layer with an effective density. Based on the law of conservation of angular momentum we suggest an equation for calculating rotation rate/speed of a granular layer in vortex apparatuses, which qualitatively and quantitatively accesses the experimental data, the accuracy being ±15%.

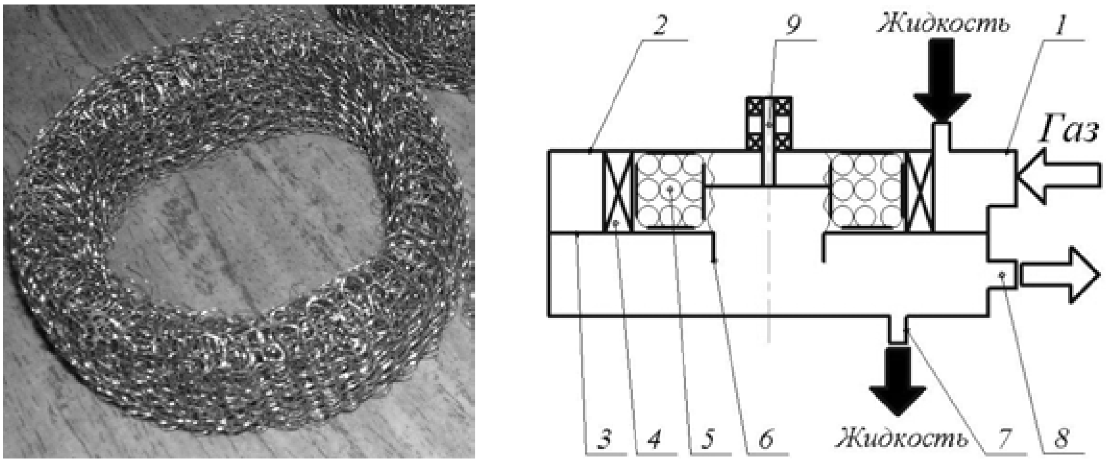


Fig. 2. a)Volumetric packing; b) Schematic of the vortex apparatus with a volumetric wire packing

As an example we present a schematic of the vortex apparatus with a solid phase made of a wire packing (Fig. 2a). If volumetric packing 5 is connected with special-designed axle 9, mounted on the bearings (Fig. 2b), it is possible to completely prevent contacts between the packing and the vortex apparatus surfaces. We derived a number of equations for calculating rotation rates of three-phase layers and pressure drops in the vortex apparatuses supplied with a low volume packing.

Our work data can be used for calculating and designing novel multiphase vortex apparatuses characterized by high (operation) intensity, small dimensions and metal consumption/weight/steel intensity.

MODELING OF CFTALYTIC α-OLEFINS OLIGOMERIZATION IN THE FLOW-TYPE REACTOR

Tsvetkov O.N.

VNII NP, 11116, Moscow, Aviamotornaya Str., 6, (495) 361-11-51, paom@rambler.ru

The possibility of modeling the α-olefin oligomerization reaction in a column flow-type reactor with a mechanical mixing device representing a multi-tier mixer with plane vanes has been discussed. The dependence of the mean residence time of the reaction mass in the apparatus on the space velocity of the flow has been experimentally found. It has been shown that the description of the oligomerization process in the said reactor by several logically acceptable kinetic models including those of: ideal reactor displacement, cascade of ideal mixing reactors, diffusional model, ideal displacement and ideal mixing reactors in succession, and visa verse, does not reveal any substantial difference in the final degree of α-olefin conversion to oligomers between the models under consideration. The reason of this may be attributed to the fact that in these computations the observed mean residence time, being a corrective factor while modeling is taken. For example, while using the ideal displacement reactor kinetic model on the kinetic parameters of decene-1 oligomerization at different temperatures a rather adequate approximation of the experimental and calculated values of the total olefin conversion to oligomers has been obtained. Given a sufficient experimental data base is available, the dependence of the yield, oligomer mean molecular mass and viscosity on the process conditions may by described by regressive equations and can be combined into a unified computer system permitting to control the oligomerization process in a flow-type reactor to produce oligomers with desired molecular-mass and viscosity characteristics. The reactor under discussion proves to be versatile for α-olefin oligomerization in the presence of pseudo-homogeneaus and homogeneaus catalyst. One of the definite advantages of the reactor consists in the combination of intensive reaction mass mixing being especially important while using pseudo-homogeneaus catalysts, providing for the required mean residence time to attain maximum possible monomer conversion.

DEHYDROGENATION OF PROPANE-ISOBUTANE MIXTURE IN A FLUIDIZED BED REACTOR OVER Cr_2O_3/Al_2O_3 CATALYST: EXPERIMENTAL STUDIES AND MATHEMATICAL MODELLING

Vernikovskaya N.V.[1,2], Savin I.G.[3], Kashkin V.N.[1], Pakhomov N.A.[1,2], Ermakova A.[1], Molchanov V.V.[1], Nemykina E.I.[1], Parahin O.A.[4]

[1]Boreskov Institute of Catalysis SB RAS, Novosibirsk 630090, Russia
[2]Novosibirsk State University, Novosibirsk 630090, Russia
[3]JSC "Tobolsk-Neftehim", Tobolsk, Russia
[4]JSC "NPK Sintez", Barnaul, Russia, E-mail: vernik@catalysis.ru

The processes of hydrocarbons dehydrogenation play an important role in the world industry of olefins production. Using fluid bed technology for hydrocarbons dehydrogenation at subatmospheric pressure has definite advantages, such as low capital and operation cost, relatively simple reactor design, continuous operation and easy process control. Fluid bed technology is successfully applied at industrial scale primarily for isobutene and isopentene production in Russian Federation and Saudi Arabia. In case of isobutene production fluid bed reactor productivity varies greatly and depends on the MTBE market demands, because isobutene produced is used further in MTBE synthesis. So, to maximize olefins productivity addition of another paraffin at the fluid bed reactor inlet looks attractive. Propane seems to be the most suitable co-feed because propene is widely used for polypropylene production.

Main goal of the present study was to predict the effect of addition of propane to the inlet reactor feed on the industrial fluid bed reactor performance.

Catalyst. A modified sample of industrial fluid bed Cr_2O_3/Al_2O_3 catalyst "KDM" (which is commercially produced by JSC "NPK Sintez", Russia) was prepared by incipient wetness impregnation of gibbsite thermal activation product [1] with an aqueous solution of CrO_3 with KOH and ZrO_2 additives [2].

Fixed bed reactor experiments and kinetics investigation. Study of the kinetics of propane-isobutane dehydrogenation was carried out using a fixed bed reactor. The reactor was a 12-mm-i.d., 130-mm-long quartz tube placed inside a sand bath. The reactor was equipped by thermocouples inside a thermowell of 6-mm o.d. installed at the reactor axis. The mixture of 0.08-0.12 mm-i.d. catalyst diluted by quartz sand was loaded into the reactor. The next operation conditions were varied: temperature, feed space velocity, propane: isobutane volume ratio, hydrogen concentration. The data obtained in the fixed bed reactor were fitted by Langmuir-

Hinselwood kinetic equations for the main reactions pathways, namely: dehydrogenation, cracking and coke formation.

Mathematical modelling of an industrial fluidized bed reactor for propane-isobutane dehydrogenation. A two-phase non-isothermal reactor model taking into account axial gas and heat dispersion was combined with kinetics and used for the industrial-scale reactor modelling.

Previous thermodynamic calculations for dehydrogenation of a model C_3–i-C_4 paraffins mixture indicate that there is a complex mutual effect of the components on the equilibrium yield of olefins [2]. Each component can act simultaneously: (i) as a diluent shifting the dehydrogenation equilibrium of the mixture components to the desired olefin and (ii) as an additional source of hydrogen, which shifts the dehydrogenation equilibrium to the left. Experiments on dehydrogenation of model C_1–C_4 paraffin mixtures on Cr_2O_3/Al_2O_3 catalysts in pilot fluidized and fixed beds show an increase of the total conversion of C_3–C_4 paraffins to olefins and an increase of the total process selectivity to olefins.

As a result of the present modelling the using propane-isobutane mixture for the industrial-scale fluidized bed olefins production at subatmospheric pressure was shown to have the following benefits:

- Selectivity to i-C_4H_8 is high enough and grows slightly from 86-87 to 90 % on increasing inlet C_3H_8 fraction from 0 to 60 % weight.
- Inlet concentrations of C_3H_8 up 20 % weight lead to the apparent selectivity to C_3H_6 exceeding 100 %. This effect arises due to i-C_4 cracking leading to additional propene formation and kinetic reasons.
- Reasonably high propene concentration of 35 % weight in C_3H_8-C_3H_6 mixture could be obtained at relatively low bed temperature 577-585 °C, allowing to obtain high olefins selectivity.
- Coke yield rises slowly (from 0.7-1.0 % weight at 100 % i-C_4 at the inlet to 1.2-1.4 % weight at 45 % C_3H_8 at the inlet) allowing safe industrial fluid bed reactor operation.

References

[1]. L.A. Isupova, Yu.Yu. Tanashev, I.V. Kharina, E.M. Moroz et al., Chemical Engineering Journal **(2005)**, 107, 163-169.

[2]. RF Patent No 2322290 / V.V. Molchanov, N.A. Pakhomov, L.A. Isupova, V.A. Balashov et al. **(2008)**, Priority of 18.12.2006.

PP-II-50

MATHEMATICAL SIMULATION OF RECYCLED FLOWSHEETS ON THE BASES OF LOW TEMPERATURE METHANOL SYNTHESIS

Vyatkin Yu.L.[1], **Beskov V.S.**[1†], **Lishiner J.I.**[2], **Malova O.V.**[2], **Nefedova T.E.**[3]

[1]*Mendeleev`s Russian University of Chemical Technology, Moscow, RF,*
yuris-vtk@mtu-net.ru
[2]*New Catalytic Technologies Ltd, Moscow, RF*
[3]*Institute of Chemical Technology, Severodonetsk, UA*

Earlier [1, 2] it was shown that methanol synthesis catalyzed by Cu-ZnO/Al_2O_3 proceeds the following two reaction routes:

$$CO_2 + 3H_2 = CH_3OH + H_2O + Q_1 \qquad K_{p1} \qquad (I)$$

$$CO_2 + H_2 = CO + H_2O + Q_2 \qquad K_{p2} \qquad (II)$$

The simplest methanol synthesis flowsheet is presented in Fig.1:

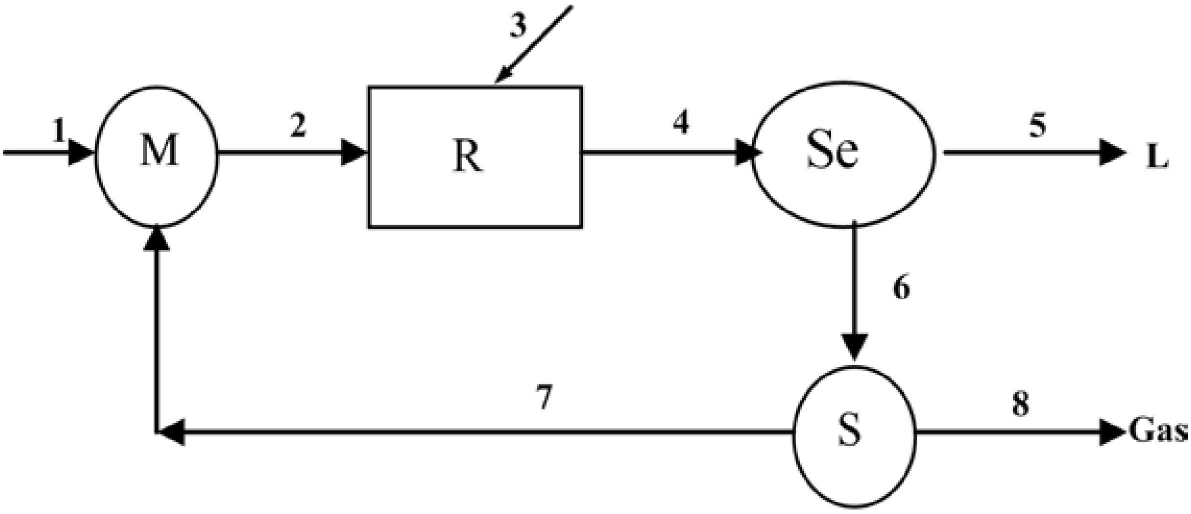


Fig. 1. Methanol synthesis flowsheet.

Here M – mixer, R – reactor, Se – separator, S – Tee, L – liquid products, gas – gas purge. Ciphers are the numbers of molar flows at appropriate points of flowsheet, $\mathbf{F_1}$, $\mathbf{F_3}$ – vector-columns of feed molar flow.

In recycle flowsheet flow 7 is unknown. There exist mathematical models of all units.

Conventional calculation procedure (procedure I) of recycle flowsheets is as follows:

1) find a cut point to transform flowsheets into ones with no recycle. That may be points numbers 2,4 or 7.

2) In consecutive order to solve mathematical models of all units.

3) iterate concentrations at a cut point. Disadvantages:

a) slow convergence of iterations;

b) calculation error is accumulated.

There is a procedure (proc. II) for simultaneous calculation of all units. Here calculation error is not accumulated, but great mathematical difficulties arise because models of units as a rule are large systems of nonlinear algebraic and differential equations. In our work we used mixed calculation procedure (proc. III). For this purpose we developed the work [3] when used $\mathbf{F_3}$ as a fictive feed. That allowed to receive linear model of flowsheet for simultaneous calculation. Iterations of concentrations are substituted by iterations of flows $\mathbf{F_3}$ due to chemical reaction.

Procedure I gives parameters for procedure II. Procedure II allows to prevent accumulation of calculation error. In our process procedure III using diminishes a number of iterations by factors 2-7.

Analytical solution for flowsheet Fig.1 showed that the value of purge flow is deter mined by not only feed flows F_1, but also by molar flows due to chemical reaction F_3. It means that even under stoichiometric mixture CO_2+$3H_2$ flowsheet feed a noncondensable CO will be accumulated in the system due to route (II). And than purge will be necessary. Suggested method due to small number of iterations allows to use comprehensive reactor models in flowsheet. We used a model of reactor with Field's tubes and reactor with radial heat and mass transfer.

References

[1]. G.I. Lin, K.P. Kotyaev, A.Ya. Rozovskii, Stud. Surf. Sci. Catal., **2000**, v.130, 713.

[2]. A.Ya. Rozovskii, Yu.B. Kagan, G.I. Lin, Kinet. and Catal., **1976**, v.17, №5, 1314.

[3]. A.J. Weißenfelder, R.E. Olson. CEP, **1980**, v.76, №1, p.40.

Acknowledgements

Authors are grateful to prof. Shmelev A.S. for valuable advices and fruitful discussion of the results of this work.

PP-II-51

CATALYTIC REVERSE-PROCESS FOR SO_2 OXIDATION: MODELLING OF THE NEW FLOW SHEETS

Zagoruiko A.N.

Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
E-mail: zagor@catalysis.ru

Utilization of sulfur dioxide in the waste gases of non-ferrous smelters is a traditionally important environmental protection problem. Usually this problem is solved by catalytic oxidation of SO_2 to SO_3 with following production of sulfuric acid. The reverse-process of sulfur dioxide oxidation, characterized with high efficiency, low capital costs and low energy consumption [1] has found a wide application in this area during last decades. Reverse-process has demonstrated a unique operation stability in case of oscillations of significant gas flow rate and temperature, typical for smelter off-gases, but improvement of operation stability and efficiency under significant oscillations of SO_2 inlet concentration and increased SO_2 inlet content (above 3-4% vol.) is still a problem.

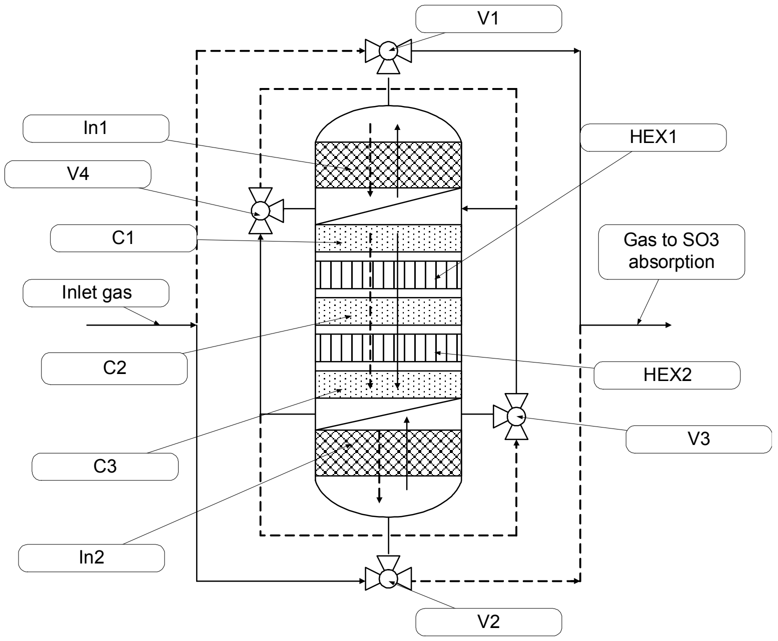


Fig. 1. Flow sheet of the process for gases with strongly variable SO_2 concentration

V – switching valves,

In – beds of inert material,

C – catalyst beds,

HEX – heat exchangers

The new flow-sheet of the reverse-process is proposed for resolution of this problem (Fig.1). In this process the reversals of the gas flow are performed only in the beds of inert heat-regenerating material, while the flow direction in the catalyst beds is kept constant [2]. Such approach provides lower maximum temperature in the catalyst bed [3], giving the way both to reduce equilibrium limitations and thus increase SO_2 conversion and to improve process stability. According to simulation data such flow sheet provides the achievement of 97-98% conversion at treatment of gases with inlet SO_2 concentration varying in the range from 2-2.5 up to 7-8% vol.

Another challenge in this area is development of reverse-processes for treatment of extra-strong smelter gases with SO_2 concentration as high as 35-40% vol. The new DC/DA reverse-process flow sheets with SO_3 recycle [4] and new version of absorption-catalytic reverse-process (Fig.2) make possible to treat such gases with overall conversion degree up to 99.96%.

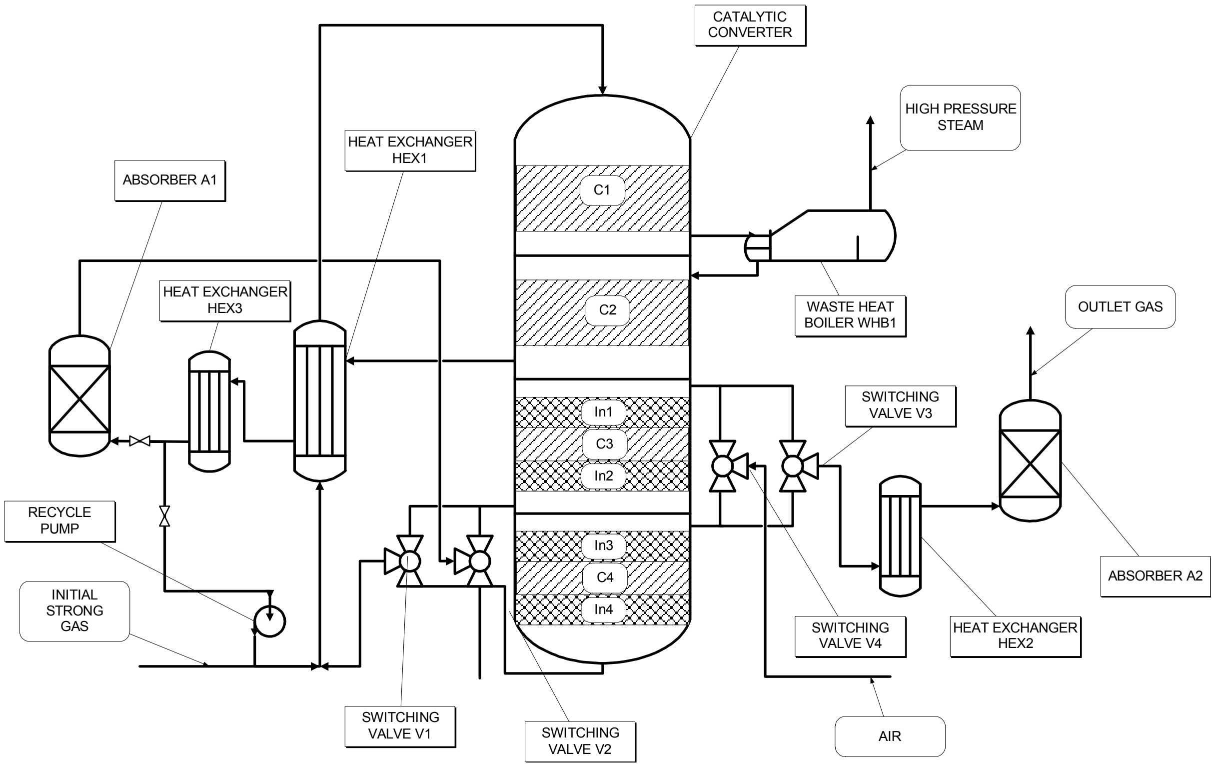


Fig.2. Absorption-catalytic reverse-process for treatment of smelter gases with SO_2 concentration up to 40% vol.

References

[1]. Yu.Sh. Matros, G.A. Bunimovich. *Catal.Rev.-Sci.Eng.*, 38(1), 1996, pp.1-68.

[2]. Russian Patent No. 2213045, 2003.

[3]. Yu.Sh. Matros, A.S. Noskov, A.N. Zagoruiko, O.V. Goldman. Theor. Found. Chem. Technol., 1994, 28(2), pp.139-144.

[4]. Eurasian Patent No. 006757, 2005.

PP-II-52

MODELING OF THE CAUNTER-FLOW EXTRACTION REACTOR OF DISPLACEMENT

Zueva Yu.N., Samoilenko N.G., Manelis G.B.

Institute of Problems of Chemical Physics, Russian Academy of Sciences.
Semenov Prospect 1, 142432, Moscow Region, Chernogolovka
E-mail: sam@icp.ac.ru

The stationary theory of the mass exchange of extraction processes developed to the present time was based on the law of chemical balance and on the simplest record of mass conservation law and served as a basis for the development of empirical method for the calculation of main parameters of the reactor at the given degree of extraction. These methods were designed on the conception of the theoretical step of contact and the volume expenses: phase's ratio. The mathematical models of the stationary theory do not take into account the hydrodynamic pictures of the process. However, the question – does the flow of phase's effect on the efficiency of the extraction process and how - has no answer.

The simple mathematical model is proposed for the counterflow extraction reactor with the ideal displacement that takes into account the flow hydrodynamics of phases in laminar approach. The analytic solution of the mathematical model is found.

The physical model is simple. The given height A solution of substance **A** (phase 1) is provided to the reactor with the given height from above. The linear rate of this phase is given. The extragent **B** (phase 2) emerges in phase 1 in the form of drops with the same size. The drop size does not change. The flow rate of this phase is known.

The analysis of the solution showed that the space distributions of phase **A** concentration significantly depended on the flow rate of the initial solution. At small flow rates of phase 1 the upper part of the reactor works, at large rates –the lower part. The interval of rates exists, when he total reactor works completely.

It was shown that at the given degree of extraction NOT at all flow rates of phase 1 the stationary regimes were realized.

ON THE TECNOLOGY OF TECHNICAL OILS FINE PURIFICATION FROM GROUP OF AROMATIC HYDROCARBONS

Ibrahimov Ch.Sh., Samedova F.I., Abbasov Kh.I.

National Academy of Sciences of Azerbaijan
Institute of Chemical Problems, Baku
xaliq-349@mail.ru

As in known, the availability of polycyclic aromatic hydrocarbons and resinous compounds in the composition of oil distillates worsens their quality.

For today the most widespread method of motor oils selective purification from aromatic hydrocarbons and resinous substances is an extraction method with the use of selective solvents. For that purpose, the polar solvents that are capable to selectively refine them are used. The experts have tested such solvents as dichloride ethyl ether, nitrobenzene, aniline, liquid sulfuric anhydride and etc. In total more than hundred solvents have been investigated. At the present main industrial solvents are phenol, furfural, and N-methyl pirromedine-2. The furfural is widely used at the Baku oil refining factories as it is less toxic and more selective, though differs with a smaller dissolvent ability.

On of the widespread devices used for clearing oils is the rotor-disk extractor that is introduced in the Baku oil refining factories as well. The scheme and its working principle are given in [1].

Another device used for oil purification is adsorber with the use of selective adsorbents. The scheme and its working principle are given in [2].

Each of the above mentioned methods of oil purification from aromatic hydrocarbons has its own essential drawback, which reduce their efficiency.

The effectiveness of the extraction method is in the fact that at large concentration of resinous and aromatic hydrocarbons it is possible to sharply reduce their concentration in the composition of the solution to be refined with the help of solvents. For example, in the oil purification experiment described in the paper [3] the distillate D-11 was used as a raw material and according to percentage ratio had the following content of hydrocarbons group in its composition:

Methane-naphthen -62,6%(masses), Aromatic: easy fraction-16,7%, Average fraction – 7,0%, Heavy fraction-7,9%, Resinous substances-5,8%.

As in seen the distillate contains more than 31% aromatic hydrocarbons. After passing 6 stages in the process of oil purification by the extraction method using furfural there remains up to 5% of aromatic hydrocarbons and resinous substances in the composition of the refined solution, which worsens the quality of oil. Continuing of oil purification further by this method is ineffective because of heavy expenses.

As to adsorption method of oil purification with the use of adsorbents, many papers proved, that at large concentration of hydrocarbons to be extracted this method is not applicable [2], as it requires heavy expenses, but at small concentration it is irreplaceable and highly effective [4,5].

As it is impossible to carry out fine clearing in the extractor, for obtaining high-quality oil from refined solution it is necessary to derive residuals of aromatic hydrocarbons and resinous substances. It is widely known that the fine purification of liquids from micro-impurities is successfully carried out by the adsorption method with appropriate selection of adsorbents. The last years researches have shown, that the best selective adsorbent for aromatic hydrocarbon derivation from the hydrocarbon mixtures is the alumina silicate adsorbent.

References:

[1]. Rudin M.G., Smirnov G.F. Projecting of oil refining and oil chemical plants. L.; Chemistry, 1984. (In Russian).

[2]. Keltsev N.V. Basis of adsorbtional techniques. M., 1984, 591 p. (In Russian).

[3]. Sheikh-zade R.I., Ponikarov S.I., Ibrahimov Ch.Sh. Experimental researches of oil processes selective purification in rotor – disk extractor. – Deposit in the Institute of the Scientific and Technical Information of the Russia (VINITI) 29.01.92, № 306-B92 (In Russian).

[4]. Samedova F.I. Greasing oils from Baku paraffin oils. Baku: «Elm» Publication, 1987, 255 p. (In Russian).

[5]. Samedova F.I. Azerbaijan oils and their ingredient composition. Baku «Elm» Publication, 2002, 247 p. (In Azeri).

PROPYLENE POLYMERIZATION AND PROPYLENE-ETHYLENE CO-POLYMERIZATION REACTORS MODELING

Reutova O.A., Gulyaev K.S., Timofeev G.S, Galyamov A.V., Demin A.M.

Omsk State University of F.M. Dostoevsky
Russia, 644077 Omsk, Pr. Mira, 55a, reutova@univer.omsk.su

The technological scheme for propylene polymerization on Ziegler-Natta (the fourth generation) catalysts is considered. Reaction proceeds consistently in following reactor cascade: the pre-polymerization reactor (R200), two liquid-phase polymerization reactors (R201 and R202), and the gas-phase reactor for propylene and ethylene co-polymerization (R401).

Computer model of consistently connected four reactors of conversion type has been constructed in UniSim Honeywell platform (fig. 1). For maintenance of demanded temperatures and pressure it is calculated auxiliaries: the heat exchangers, the pumps, the compressor, the valves.

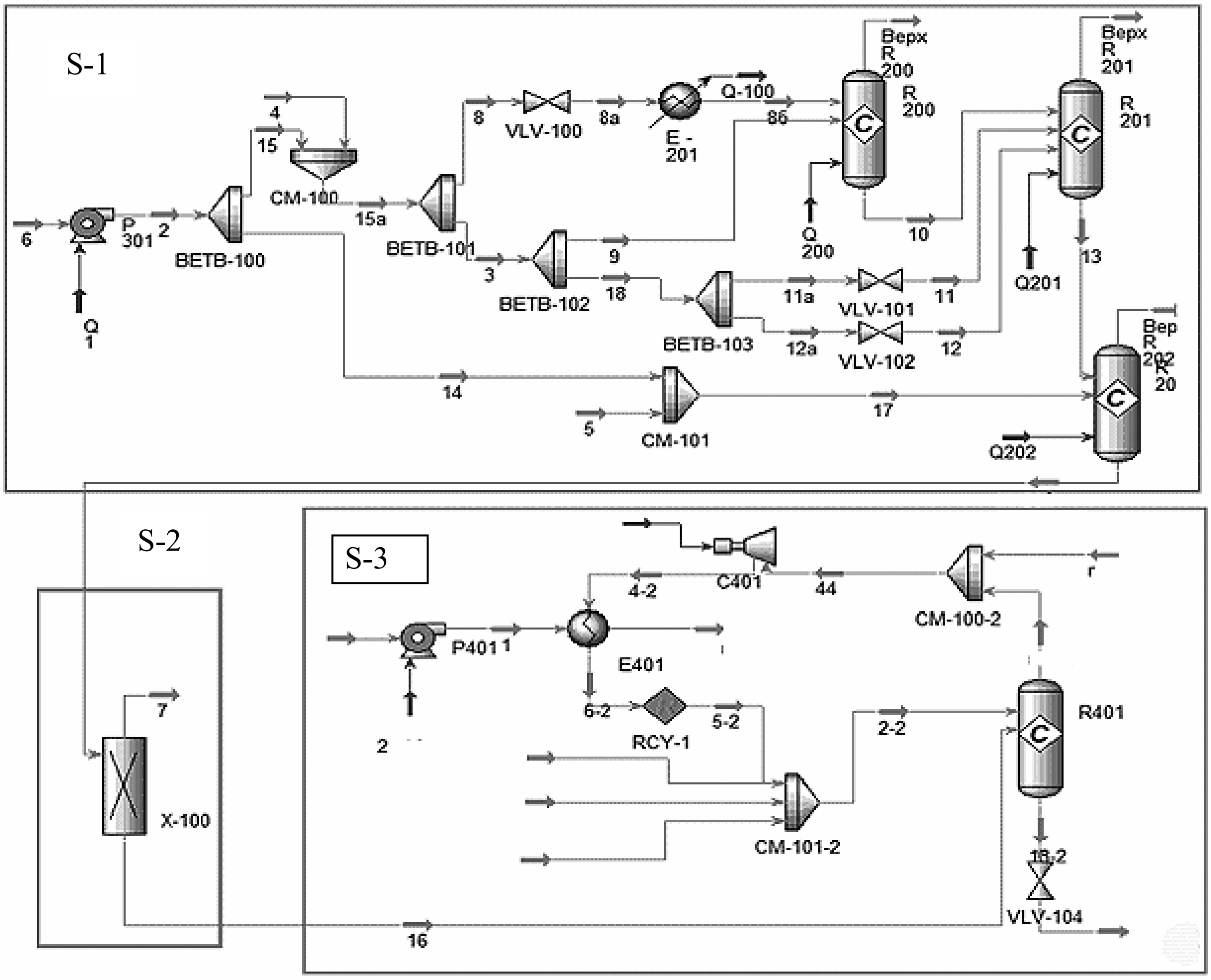


Fig. 1 Computer model for propylene polymerization reactors

Polymerization in reactors R200, R201 and R202 proceeds in the environment of liquid phase with hydrogen addition. Co-polymerization reaction proceeds in the gas-phase reactor on "living" polymer with ethylene and propylene. Contact time is 120 minutes.

The change of transformation degree onto the reactors cascade is constructed on the basis of computer model. Also the temperature profile on the reactors cascade is constructed (fig. 2). The isothermal mode is supported.

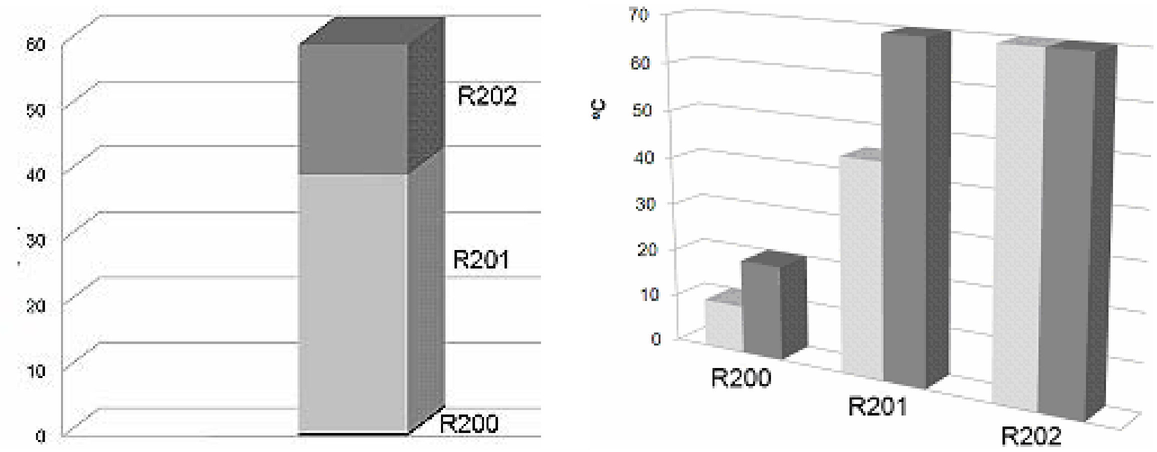


Fig. 2 The transformation degree and the temperature profile on the reactors cascade

The pre-polymerization proceeds under the lower temperature because a part of the active centers is deactivated irreversible under the raised temperature.

Catalyst introducing into a reaction zone at polymerization temperature 70°C leads to the formation of polypropylene with the lowered bulk density. The possible reason of this phenomenon is partial or a final fracture of a catalyst particle during the intensive beginning of polymerization.

The catalyst introducing into polymerization phase under the lowered temperature and the carrying out pre-polymerization under the soft conditions provide the demanded bulk density of polypropylene. The temperature into R201 and R202 reactors is supported at level 70°C.

On the basis of computer experiments the dependence of the gas phase composition is constructed at temperature change in liquid-phase reactors. Under temperature 75°C the propylene passes from a liquid phase in the gaseous one.

REACTOR FOR LIQUID-PHASE PROCESSES ON FIBROUS CATALYSTS AND SORBENTS

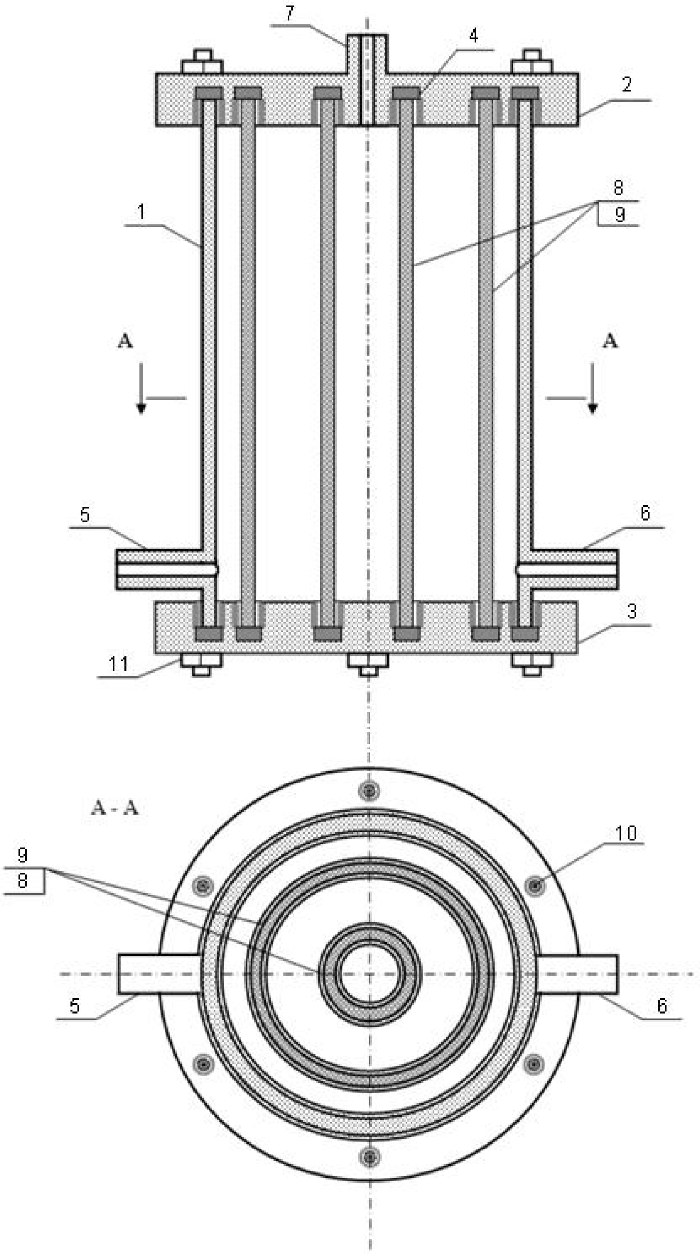
**Yegiazarov Yu.G., Cherches B.Kh., Radkevich V.Z.,
Potapova L.L., Guterman I.D.**

*Institute of Physical-Organic Chemistry of the National Academy
of Sciences of Belarus, 13, Surganov St., Minsk 220072, Belarus
E-mail: yegiazarov@ifoch.bas-net.by*

In recent decades development of new types of catalytic systems and sorbents on the basis of fibrous materials is gaining more attention from many researchers. Main advantages of fibers are their developed surface and physicochemical properties, which intensify catalytic and sorption processes. But advantages are usually accompanied with disadvantages, in the case of hydrophilic fibrous ion exchangers it's high hydraulic resistance of swollen material layer. High hydraulic resistance is hindering liquid-phase processes in traditional chemical reactors, thus limiting industrial use of fibrous ion exchangers.

We've designed and made pre-production model of reactor for processes with fibrous catalysts and sorbents. Assembled representation of developed catalytic reactor is depictured at Pic. 1: elevation drawing (vertical section) and vertical view (horizontal section). Reactor consists of body 1, upper and lower flanges 2,3 with rabbets for densifier 4. There are two diametrically opposite inlet nozzles 5 and 6 at the lower part of the reactor. Outlet nozzle 7 is located in the center of the upper flange. Two porous pipes 8 and 9 were coaxially arranged inside body of catalytic reactor. Fibrous ion exchanger is placed between these pipes. Reactor body and pipes are gripped between upper and lower flanges with hanger bolts 10 and screw nuts 11. All reactor components, except for hanger bolts and screw nuts, are made of polymeric materials.

Developed reactor was tested in the process of catalytic water deoxygenating [1]. Fibrous anion exchanger with supported palladium was used as catalyst. Water stream with dissolved hydrogen was injected in the reactor though inlet nozzles, then water radially passes through palladium supported fibrous catalyst placed between porous pipes. Deoxygenized water comes out from outlet nozzle. Overall result of reactor and process tests was positive.



Pic. 1. Scheme of chemical reactor with radial raw material injection.
1 – reactor body; 2,3 – flanges; 4 – rabbets for densifier; 5,6 – inlet nozzles,
7 – outlet nozzle; 8,9 – porous pipes; 10 – hanger bolt; 11 – screw nut.

Reactor design described above provides for radial injection of raw material (water in our case) into reaction zone, which allows decrease thickness of fibrous catalyst or sorbent layer and, thus, lower its hydraulic resistance.

References

[1]. Yegiazarov Yu.G. // Energeticheskaya strategiya. **2009**. N 3. P. 52-67.

PP-II-56

MODELING OF CATALYTIC MICROREACTORS FOR NAPHTHA STEAM REFORMING

Mustafa Karakaya, **Ahmet K. Avci**

Department of Chemical Engineering, Bogazici University, Bebek 34342,
Istanbul, Turkey, avciahme@boun.edu.tr

This study involves comparison of two microreactor configurations, the multiple adiabatic bed (MAB) and the microchannel reactors, to produce hydrogen needed to drive a 2-kW PEM fuel cell. In the MAB system, composed of adiabatic catalytic packed beds and microchannel heat exchangers interconnected to each other, hydrogen is produced via steam reforming (SR) of *n*-heptane, model compound for naphtha, in a number of adiabatic reactors packed with a Ni-based catalyst. Heat requirement of endothermic SR is supplied by exothermic combustion of methane running in a separate array of adiabatic reactors packed with a Pt-based catalyst. Heat transfer between the two reactions is achieved in microchannel heat exchangers that connect the effluent streams of the combustion and reforming beds. Upon heat exchange the streams are fed to the successive adiabatic beds and the reaction-heat exchange cycle is repeated until the desired amount of hydrogen is produced [1,2].

The second configuration, microchannel reactor, has parallel, identical channels with dimensions in the sub-millimeter range and is characterized by laminar flow conditions. The microchannel reactor design in this study involves *n*-heptane SR in channels whose walls are coated by a Ni-based catalyst. Heat needed to drive SR is supplied by methane combustion running in parallel channels coated with a Pt-based catalyst. Sets of parallel, straight channels, all of which have identical square cross-sections, are etched on metallic plates and coated with either a Ni- or Pt-based catalyst. The plates are then bonded on top of each other so as to form an alternating stack of endothermic and exothermic channels. Heat transfer between the channels of the same plate is assumed to be negligible, allowing the multichannel system to be characterized by a representative unit involving a single pair of exothermic and endothermic channels separated by a metallic wall. The system operates at steady state and counter-current flow of reactive streams is considered.

The representative microchannel unit is modeled by 2D continuity, momentum, energy conservation and species mass transport equations for the fluid and catalytic washcoat phases, and energy conservation equation for the steel wall. The reactive streams are assumed to be incompressible Newtonian fluids. Simultaneous solution of these equations is carried out using the method of finite elements under Comsol Multiphysics environment. Numbering-up the channels, i.e. sizing of the microchannel reactor is handled by dividing the basis flow rate (which is 2.2×10^{-2} mol s^{-1} of hydrogen equivalent to 2-kW PEMFC power [3]) by the corresponding single-channel flow rates due to the assumption of flow equipartition.

Modeling of the reactors and heat exchangers involved in MAB system are decoupled; one-dimensional, steady-state, pseudohomogeneous fixed-bed models are used to simulate adiabatically operating beds. The resulting set of ordinary differential equations is solved in MATLAB environment. The microchannel heat exchangers are of the same design as the microchannel reactor described above, i.e. alternating stack of hot- and cold-stream channels etched onto metallic plates, with the single exception of catalytic washcoats, hence absence of species transport. Solution of the 2D steady-state transport equations is handled using Comsol Multiphysics. The design procedure is of trial-and-error nature; reactor array design that involves sizing and numbering precedes interstage heat exchanger design [2].

Saw-tooth shaped, controlled temperature profiles are obtained along the reactor arrays of the MAB system, while temperatures in the SR and combustion channels of the microchannel reactor equilibrate rapidly down the channel length due to high heat transfer rates. As for sizing, the MAB configuration consisting of 9 combustion beds, 9 reforming beds and 9 microchannel heat exchangers, occupies a volume of 1.39×10^{-3} m^3, 81% of which is contributed by the SR reactors. 14450 microchannels required to produce the stated amount of hydrogen occupy a volume of 1.04×10^{-3} m^3.

References

[1]. E.L.C. Seris, G. Abramowitz, A.M. Johnston and B.S. Haynes, Chem. Eng. J., 135S (2008) S9.

[2]. A.K. Avci, D.L. Trimm, M. Karakaya, Catal. Today doi:10.1016/j.cattod.2009.01.046.

[3]. O. Tan, E. Masalaci, Z.I. Onsan, A.K. Avci, Int. J. Hydrogen Energy, 33 (2008) 5516-5526.

Acknowledgements

Financial support is provided by Bogazici University through project BAP-09HA507D. A.K. Avci acknowledges TUBA-GEBIP program.

MATHEMATICAL MODELING OF BENZENE HYDROGENATION IN THE THIOPHENE PRESENCE UNDER PERIODIC OPERATION

Reshetnikov S.I.[1], **Pyatnitsky Yu.I.**[2], **Ivanov E.A.**[1], **Dolgykh L.Yu.**[2]

[1]Boreskov Institute of Catalysis SB RAS, Pr. Akademika Lavrentieva 5,
Novosibirsk, 630090, Russia, E-mail: reshet@catalysis.nsk.su
[2]Pisarzhevsky Institute of Physical Chemistry NASU, Prospekt Nauky, 31,
Kiev, Ukraine; ldolgykh@inphyschem-nas.kiev.ua

One of the important subjects of environmental catalysis is research on clean fuels [1,2]. In the past decade, some areas of the research on clean fuels included hydrodearomatization (HDA) and hydrodesulfurization (HDS), which proceed on sulfide (Ni,Mo) and (Ni, W) catalysts. The new Environmental Protection Agency (EPA) regulations reduce the sulfur content of the highway diesel fuel from 500 ppmw (1989) up to 15 ppmw (June 2006). In this case, the volume of catalyst bed will have to be increased 3.2 times as that of the current HDS catalyst bed [2]. Therefore, new catalysts and processes of fuels treatment are necessary. As it is well known, a difficult problem of the HDA–HDS processes on sulfide catalysts is the mutual inhibition of hydrogenation reactions by sulfur–organic compounds and of hydrogenolysis reactions by aromatics.

At the same time, experimental and theoretical studies in heterogeneous catalysis during the last decades have given evidence that reactor performance under unsteady state conditions can lead to improved process efficiency compared to steady state operation. Under transient conditions, it is possible to maintain the catalyst surface in an optimal state increasing the average reaction rate and selectivity towards a specific product resulting in an enhanced reactor performance. One of the ways to attain the catalyst unsteady state is forced oscillations of the reactant concentrations (periodic reactor operations) [3,4].

The HDA–HDS problem in this work was studied on the example of benzene hydrogenation and thiophene hydrogenolysis:

$C_6H_6 + 3H_2 = C_6H_{12}$ (benzene hydrogenation), HDA,

$C_4H_4S + 4H_2 = H_2S + C_4H_{10}$ (thiophene hydrogenolysis), HDS

The goal of this work is mathematical modeling of benzene hydrogenation into cyclogehane in the thiophene presence over the sulfide Ni-Mo/γ-AL_2O_3 catalyst under periodic operation.

The reactant concentration in the reactor feed is periodically varied in the form of a square wave function. In the first part of a period, the concentration corresponds to the hydrogen + benzene mixture and then, the flow was replaced by a flow of hydrogen + thiophene (or hydrogen + benzene + thiophene) in the second part of a period. The split between the two parts of a period is defined by the parameter γ. For $\gamma = 0$, the reactor is operated under steady-state with a constant feed concentration.

The modeling was performed with the use of the mathematical model of the continuous stirred tank reactor. For modeling was used the unsteady state kinetic model, which describes well the dynamics of changes in the benzene conversion with presence and absence thiophene [5]. Kinetic of both benzene hydrogenation and thiophene hydrogenolysis on sulfide Ni-Mo/γ-Al_2O_3 catalyst includes 7 steps. The model has been developed assuming that the catalyst surface contains only one type of active sites - nickel atoms found in the sulfide bimetallic complex - on which the reactions of hydrogenolysis of bond C-S and benzene hydrogenation occur.

On the base of the kinetic model, the theoretical analysis of the reactor performance under unsteady state conditionswas carried out. The unsteady state conditions on the catalyst surface are supposed to be created by forced oscillations of concentration of thiophene in the reactor inlet. The influence of various parameters like cycle split, length of forced oscillations period in the reactor was investigated with respect to the conversion of the benzene. The optimal cycle split is 0.1, the length of forced oscillations period in the reactor consists of 300 min. It is shown that under periodic reactor operation an average benzene conversion can be up to several times higher than the steady state value.

References

[1]. B.H. Cooper, B.B.L. Donnis: *Appl. Catal. A: General*, **1996,** 137, 203.

[2]. C. Song, X. Ma. *Applied Catalysis B*: **2003,** 41, 207.

[3]. P.L. Silveston, R.R. Hudgins, A. Renken, Catal. Today. **1995**, 25, 91.

[4]. S.I. Reshetnikov, E.A. Ivanov, L. Kiwi-Minsker, A. Renken, Chem. Eng. Technol. **2003,** 26, 751.

[5]. E.A. Ivanov, S.I. Reshetnikov, M.V. Sydyakin and A.N. Startsev. *React. Kinet. Catal. Lett.* **2006**, 88, 399.

Acknowledgements

The authors acknowledge to RFBR (Grant № 09-03-90406-Ukr_f_a) and FRSF (Grant № F28/267-2009) for the financial support.

HONEYCOMB CATALYSTS WITH POROUS WALLS: CFD MODELING OF TRANSPORT PHENOMENA AND EXOTHERMIC REACTION AT SHORT CONTACT TIMES

Klenov O.P.[1], Chumakova N.A.[1,2], Pokrovskaya S.A.[1,2], Noskov A.S.[1]

[1]*Boreskov Institute of Catalysis SB RAS, Novosibirsk, 630090 Russia,*
E-mail: klen@catalysis.ru
[2]*Novosibirsk State University, Novosibirsk, 630090 Russia*

Structured catalyst systems are promising for many applications. For design purposes the data concerning the effects of transport phenomena on the reaction proceeding are necessary. The simplified models do not always show all features of hydrodynamic processes in such systems, while CFD modeling makes available more details [1, 2].

Here the results of theoretical investigation of the transport phenomena under conditions of an exothermic catalytic reaction in a porous honeycomb catalyst are presented. The influence of inhomogeneity of reacting gas flow on the reaction performance at the surface and in the volume of the catalyst is considered.

To obtain the spatial distribution of a laminar reacting gas flow in the honeycomb catalyst with triangular channels, the complete system of Navier-Stokes equations is solved by using the software FLUENT. A monolith fragment is considered containing single channel whose walls are permeable for the flow; the feed contains methane and oxygen. Catalytic methane oxidation is under study as an example. The operation conditions and porous structure parameters are varied for inlet temperature of 400-700°C.

The local transfer rates over the channel surface are studied at 4-8 ms contact time. For the conditions under study inhomogeneous distribution of gas flow velocities is observed also. As usual, the highest values of the transfer rates are observed in the middle parts of the channel sides, and the reduced values in the regions near the edges are related to the formation of boundary layers. Maximum transfer intensity near the inlet is higher comparing with an impermeable monolith due to the gas flow penetration through the frontal catalyst surface.

The distribution of catalytic reaction rates, methane concentrations and temperatures are determined in the catalytic system: in gas flow, at the outer surface and inside the porous catalyst. The distribution of CH_4 transformation rate over the channel surface along the monolith length follows the local transfer rates, maximal reaction rate is observed in the initial thin layer of the catalyst volume and in the part of frontal surface layer. The temperature distribution has heterogeneous character both in the gas flow and in the catalyst volume increasing rather smoothly in the gas volume, the temperature difference between the catalyst and gas volumes is significant. The character of local methane concentration and temperature profiles in the gas phase are similar (Fig.1).

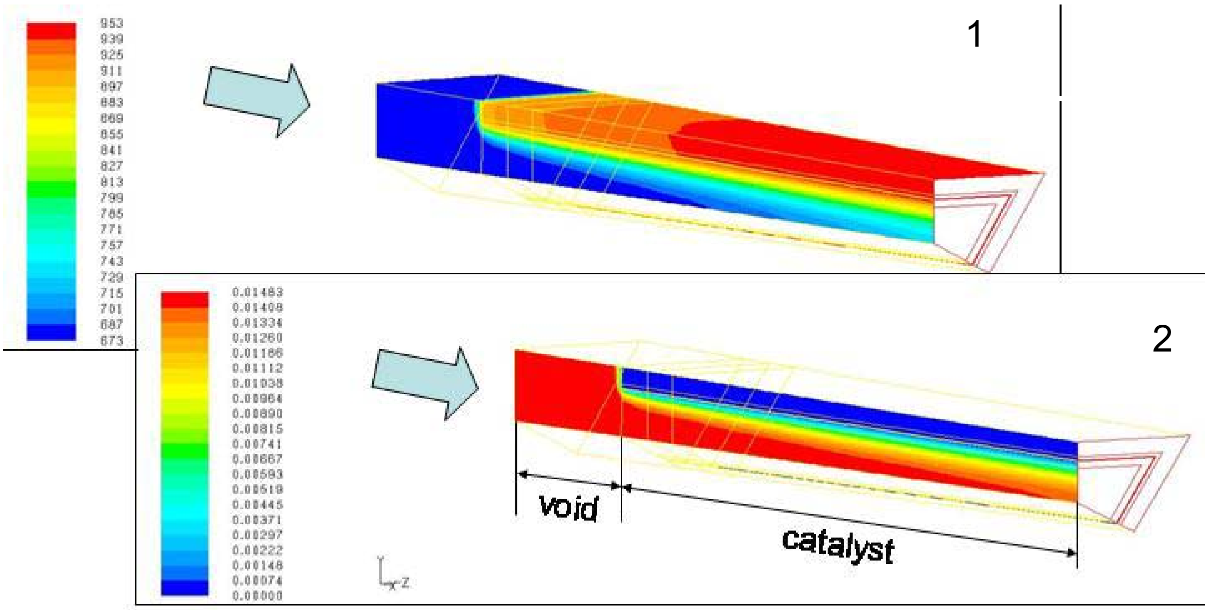


Fig. 1. Distribution of temperature (1) and CH_4 concentration (2) along the catalyst fragment length. Inlet temperature and CH_4 concentration are equal of 400°C and 1.5% vol. correspondingly.

Thus, results of CFD modeling show that the performance of an exothermic catalytic reaction in the structured catalyst with porous walls is characterized by significant inhomogeneity of the reaction rate and temperature in the catalyst volume.

References

[1]. S. Tischer, C. Correa, O. Deutschmann. Transient three-dimensional simulations of a catalytic combustion monolith using detailed models for heterogeneous and homogeneous reactions and transport phenomena. - Catalysis Today **(2001)** Vol. 6**9**, No. 1-2, pp. 57-62.

[2]. O.P. Klenov, S.A. Pokrovskaya, N.A. Chumakova, S.N. Pavlova, V.A. Sadykov, A.S. Noskov. Effect of mass transfer on the reaction rate in a monolithic catalyst with porous walls. - Catalysis Today **(2009)** Vol. 144, No. 3-4, pp. 258-264.

POSTER PRESENTATIONS

SECTION III

SECTION III-A + SECTION III-B

MICRO-REACTORS FOR SPACE PROPULSION APPLICATIONS: MONOLITHIC FOAM CATALYSTS

Amrousse R.*, **Batonneau Y., Farhat K., Kappenstein C.**

LACCO (Laboratoire de Catalyse en chimie Organique), Poitiers 86022, France
**Corresponding author: rachid.amrousse@univ-poitiers.fr*

Open-cell ceramic foams on cordierite ($2MgO\cdot 2Al_2O_3\cdot 5SiO_2$) and silice carbide (SiC) with pore counts between 20 and 30 PPI (Pores Per Inch) (Figure 1) were studied in connection with their morphology have gained interest in the last decade due to their potential applications as carriers in various processes. Their properties such as low pressure drop, high surface area enhancing mass transport, as well as the radial mixing in the tortuous structure, improving heat transfer in highly endothermic and exothermic reactions, make them attractive in many research fields. They have already been used in several applications such as waste and exhaust gas purification [1, 2, 3], methane and propane combustion, carbon dioxide reforming, partial oxidation of hydrocarbons at short contact times, preferential oxidation of carbon monoxide in hydrogen and Fischer–Tropsch-synthesis [4]. Most of these applications involve high flow rates and/or high reaction rates, typically controlled by external mass and heat transfer. The knowledge of mass (and heat) transfer and pressure drop properties of these reticulated structures is therefore of extreme importance for reactor design and industrial implementation.

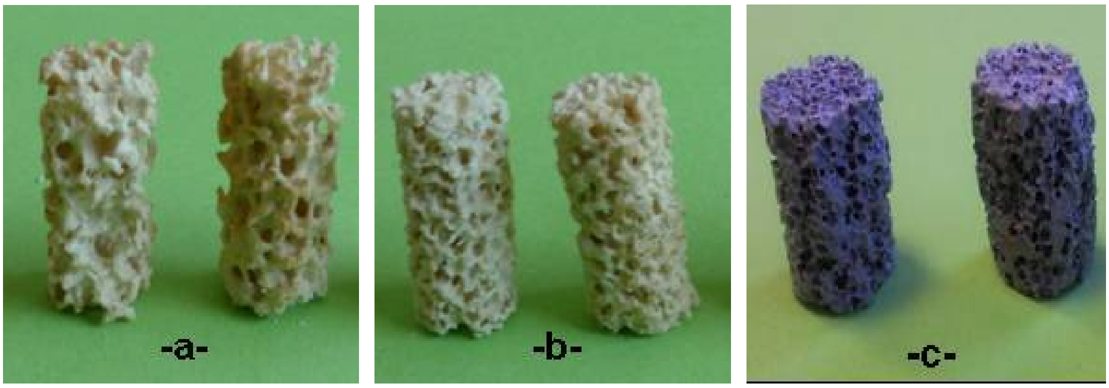


Figure 1: The received monolith foams (9 mm in diameter and 20 mm in lenght), cordierite 20 ppi (a), 30 ppi (b) and silice carbide 30 ppi (c).

The focus of this work is therefore to prepare the monolithic faom catalysts based on noble metals (Ir, Pt, Rh and Ir) for ignition of cold H_2/O_2 mixtures. The prepared monolith faom catalysts are characterized by physico-chemical techniques (X-ray diffraction, Scanning electron microscopy, nitrogen physisorption, …etc).

References

[1]. A.N. Pestryakov, E.N. Yurchenko, A.E. Feofilov, Foam-metal catalysts for purification of waste gases and neutralization of automotive emissions, Catalysis Today, Vol. 29, 1996, pp. 67-70.

[2]. N. Russo, D. Fino, G. Saracco, V. Specchia, Studies on the redox properties of chromite perovskite catalysts for soot combustion, Journal of Catalysis, Vol. 229, 2005, pp. 459-469.

[3]. B.A.A.L. van Setten, C.G.M. Spitters, J. Bremmer, A.M.M. Mulders, M. Makkee, J.A. Moulijn, Stability of catalytic foam diesel-soot filters based on Cs_2O, MoO_3, and Cs_2SO_4 molten-salt catalysts, Applied Catalysis B: Environmental, Vol. 42, 2003, pp. 337-347.

[4]. C.S. Chin, H. Lee, Formation of metal–carbon σ-bonds via reactions of alkynes with iridium and their reactivity toward carbon–carbon bond formation with neighboring hydrocarbyl ligands, Comptes Rendus Chem, Vol. 8, 2005, pp. 1386-1391.

Acknowledgements

The research was conducted in the Laboratory of Catalysis and Organic Chemistry (LaCCO, Poitiers, France) and funded by French Spatial Agency (CNES, Centre National d'Etudes Spatiales, Evry, France).

PP-III-2

EFFECT OF ACID CATALYST ON THE COMPOSITION OF THE LIQUID FRACTION OBTAINED IN TIRE PYROLYSIS

Arabiourrutia M.[1], López G.[2], Aguado R.[3], Olazar M.[4], Bilbao J.[5]

[1]University of the Basque Country/Chemical Engineering Department,
PO Box 644– 48080 Bilbao, (Spain), E-mail: miriam.arabiourrutia@ehu.es
[2,3,4]University of the Basque Country/Chemical Engineering Deparment

The large quantity of used tire generated is increasing continuously. The forecast for 2012 is that world generation will exceed 17 million tonnes. This makes the valorization of used tires more interesting, and among the different technologies, pyrolysis is considered to be one of the more feasible solutions that may be economically profitable at large scale [1].

This paper conducts a study on the in situ use of acid catalysts in the pyrolysis of tires in a conical spouted bed reactor, with the aim of exploring the effect of the catalyst properties on the composition of the liquid fraction.

The raw material is standard tire rubber containing approximately 30% of natural rubber, 30% of styrene-butadiene rubber and 30% of carbon black. The remaining 10% is made up of sulphur, zinc oxide and additives for obtaining a suitable vulcanization. The experiments have been carried out in a conical spouted bed reactor. This reactor is especially suitable for flash pyrolysis [2], given that the gas residence time is very short. The two catalysts used have been prepared based on HZSM-5 and HY zeolites, which have been supplied by Zeolyst International. The experiments have been carried out at 500 °C. The tire has been fed in pulses of 2g into a 15 g catalytic bed. The volatile product fractions monitored are: C_1-C_4 gases (with CO and CO_2), non aromatic C_5-C_{10} fraction, aromatic C_{10-} fraction and C_{10+} (tar). In Table 1 are shown the percentages in mass of different lumps of compounds that formed the liquid fraction obtained in thermal and catalytic pyrolysis at 500 °C.

As it can be observed, the percentage of C_5-C_{10} fraction decreases considerably in the catalytic pyrolysis, especially in the case of HY catalyst. This decrease has as consequence the increment in aromatic and tar fractions. In the case of HZSM-5 catalyst this decrease is not so important and the percentage of tar fraction also decreases.

Table1. Percentages of different lumps, in mass.

Lumps	Thermal pyrolysis	Catalytic pyrolysis with HZSM-5	Catalytic pyrolysis with HY
C_5-C_{10} fraction	46.96	38.6	11.04
C_5 isoprene	6.82 5.21	19.91 10.73	2.37 10.73
C_6	1.23	4.44	1.05
C_7	1.02	2.63	1.01
C_8	2.19	1.21	0.48
C_9	0.76	0.22	0.12
C_{10} dl-limonene	34.94 25.53	10.19 7.68	6.01 3.82
Aromatic fraction C_6-C_{10}	12.30	28.59	36.66
Tar (C_{10+})	40.74	32.81	52.30

This different product distribution obtained with HZSM-5 and HY catalyst is a consequence of the higher micropore size of the HY zeolite (7.8 Å versus 5.6 Å of HZSM-5 zeolite), which gives way to a higher proportion of aromatic compounds.

If we focus on the composition of aromatic fraction, in the case of HZSM-5 zeolite the most abundant compounds are benzene, toluene and xylenes, while in the case of HY zeolite C_9 and C_{10} benzene derives and naphthalene are in higher proportion. With respect to tar fraction, in thermal pyrolysis PAH represents only 2.42%, with HZSM-5 catalyst 6.23% and with HY catalyst increases until 34.25% in mass.

References

[1]. Williams P.T.; Brindle A. J. *J. Anal. Appl. Pyrolysis*, *67*, 2003, 143-164.

[2]. Olazar M., Aguado R., Velez D., Arabiourrutia, M. & Bilbao, J., *Ind. Eng. Chem Res.*, 44(11), 2005, 3918-3924.

Acknowledgements

This work was carried out with the financial support of the University of the Basque Country (Project GIU06/21)and the Ministry of Science and Education of the Spanish Government (Project CTQ2004-01562/PPQ).

PP-III-3

GLYCEROL CRACKING REACTION OVER Ni AND Co CATALYSTS: EFFECTS OF METAL LOADING AND CERAMIC SUPPORTS

Atong D.[1], Thassanaprichayanont S.[1], Pechyen C.[2], Sricharoenchaikul V.[3]

[1]National Metal and Materials Technology Center, Thailand science Park,
Pathumthani, 12120, Thailand
[2]Department of Packaging and Materials Technology, Faculty of Agro-Industry,
Kasetsart University, Bangkok, 10900, Thailand
[3]Department of Environmental Engineering, Faculty of Engineering, Chulalongkorn
University, Bangkok, 10330, Thailand, viboon.sr@chula.ac.th

During conversion of vegetable oils into biodiesel, about 10 wt.% of glycerol is produced as a byproduct. With increase in production of biodiesel, huge surplus of glycerol is expected in the world market and therefore, it is essential to find useful applications for glycerol. The upgrading of glycerol can be carried out through different techniques, depending on the final products required. Finding new applications for glycerol will increase the economy of the whole biodiesel production process [1,2]. In this work, preparation and testing of nickel and cobalt catalysts for glycerol cracking reaction were carried out using the impregnation method on various supporters, such as alumina, titanium oxide, and dolomite. The overall specific surface area of Al_2O_3, TiO_2, and dolomite supported catalysts measured by BET were in the range of 7-14 m^2/g, 7-11 m^2/g and 6-16 m^2/g, respectively. From SEM images (Figure 1), using wetness impregnation method resulted in a fairly uniform macroscopical distribution of the nickel and cobalt. The amount of nickel and cobalt loadings on the catalysts from EDS were 8-11.5 and 6-13.3 wt %, respectively.

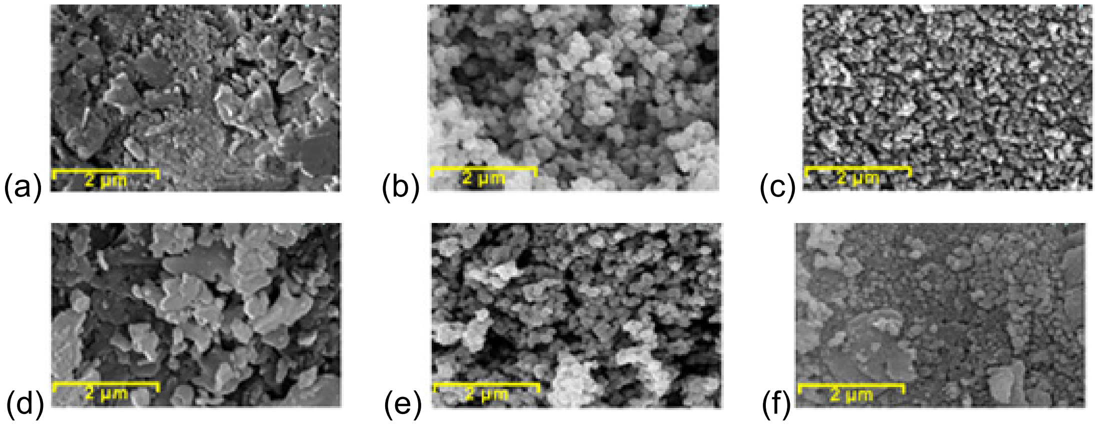


Fig. 1. SEM images of support and synthesized catalysts (a) 10%Ni/Al_2O_3, (b) 10%Ni/TiO_2, (c)10%Ni/dolomite, (d) 10%Co/Al_2O_3, (e) 10%Co/TiO_2, and (f) 10%Co/dolomite.

The catalytic performance of prepared catalysts was evaluated by the conversion of waste glycerol using a fixed bed quartz reactor. Catalytic activity on glycerol conversion for the reaction at 700°C was higher for Ni based catalysts than those of Co based ones. Higher Ni loading from 5 to 10wt% also enhanced gas production rate (Figure 2). Both Ni and Co catalysts exhibited significant deactivation with time. Types of supporter were significant to catalytic performance for the case of Ni catalysts. For comparison between supports with regards to carbon and hydrogen conversion using 10%wt.Ni and 10%wt.Co loading, the order was as follows: TiO_2>Dolomite>Al_2O_3>no catalyst. On the other hand, for using 5%wt.Ni loading, the order of the performance was as follows: Al_2O_3≈Dolomite>TiO_2>no catalyst. The highest lower heating value of product gas and H_2 to CO ratio obtained when using 10%Ni/TiO_2 and 10%Ni/Al_2O_3, respectively (Figure 3).

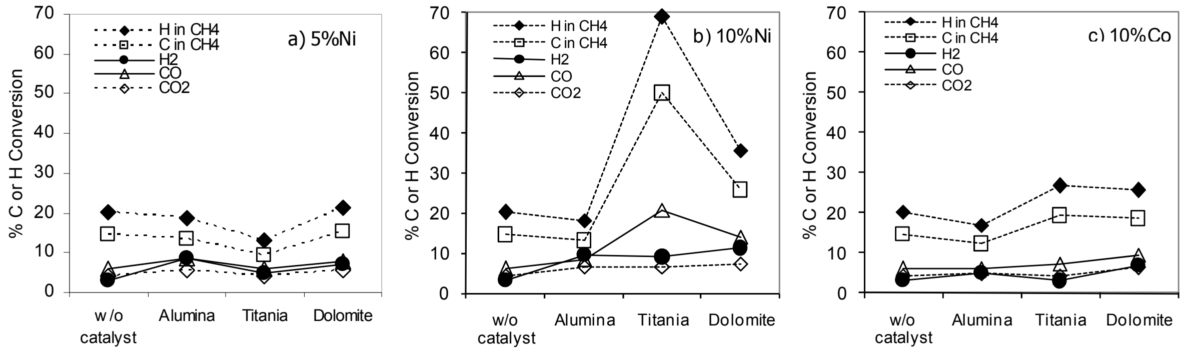


Fig. 2. Effect of support on gas produced from catalytic reforming of glycerol using: (a) 5%wt. of Ni, (b) 10%wt. of Ni and (c) 10%wt. of Co.

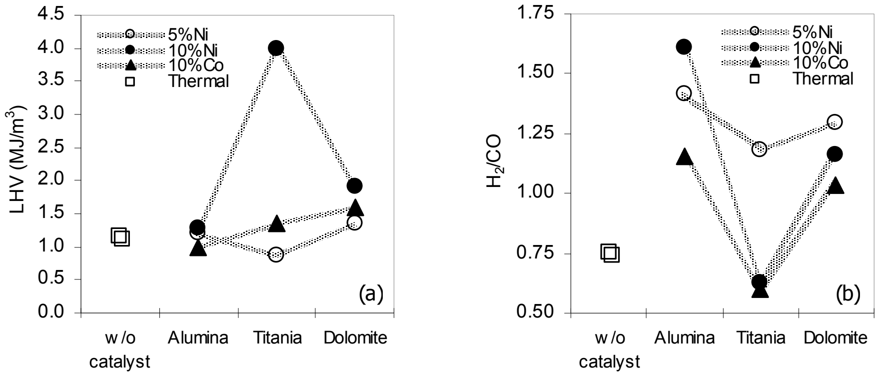


Fig. 3. Quality of product gas: (a) lower heating value (LHV) and (b) H_2/CO ratio from various catalytic reactions at 700°C.

References

[1]. Fernández, Y., Arenillas, A., Díez, M. A., Pis, J. J. and Menéndez, J. A., Pyrolysis of glycerol over activated carbons for syngas production, Journal of Analytical and Applied Pyrolysis, Vol. 84 (2009), pp. 145-150.

[2]. Adhikari, S., Fernando, S. and Haryanto, A., Production of hydrogen by steam reforming of glycerin over alumina-supported metal catalysts, Catalysis Today, Vol. 129 (2007), pp. 355–364.

PP-III-4

OPTIMAL CONDITION OF GLYCEROL STEAM REFORMING FOR DIFFERENT TYPES OF PEMFC

Authayanun S. and **Arpornwichanop A.**

Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand, Amornchai.A@Chula.ac.th

Proton exchange membrane fuel cell (PEMFC) is an electrochemical conversion device that can efficiently generate electrical power with a wide range of applications. In general, PEMFC can be divided into two types depending on its operating temperature range: low temperature PEMFC (LT-PEMFC) (60-80 °C) and high temperature PEMFC (HT-PEMFC) (100-200 °C). Due to its low temperature operation, the LT-PEMFC requires higher purity of H_2 than the HT-PEMFC. The content of CO in H_2 feed for LT-PEMFC is limited to be less than 10-50 ppm [1] whereas HT-PEMFC can tolerate CO up to 2-5% at 180 °C without the degradation of cell performance [2]. As a result, a reforming process for H_2 production is different for the two types of PEMFC. A purification unit in the reforming process is necessary for LT-PEMFC. In contrast, reforming gas can be directly fed to HT-PEMFC without CO removal processes.

The aim of this study was to find an optimal condition of a steam reforming process for both the LT-PEMFC and HT-PEMFC. Glycerol as a byproduct derived from biodiesel production was considered to be a renewable fuel for the production of hydrogen. From the thermodynamic analysis, it was found that for LT-PEMFC, the highest amount of H_2 from a glycerol steam reformer integrated with a water gas shift reactor is obtained at the temperature of 1000 K and the steam to glycerol molar ratio of 3. An increase in operating temperatures and steam to glycerol ratio slightly enhances H_2 content but reduces CO content. In case of HT-PEMFC, the reformer is needed to be operated at lower temperatures and high steam to glycerol ratio to produce H_2 with the concentration of CO less than 2-5%. The result also reveals that the steam reformer can operate at higher temperatures to give more hydrogen yield if higher content of CO in reforming gas is allowed. Fig. 1 shows the boundary of opearating conditions as a basic tool for designing a HT-PEMFC reforming process to generate H2 with specified CO limitation.

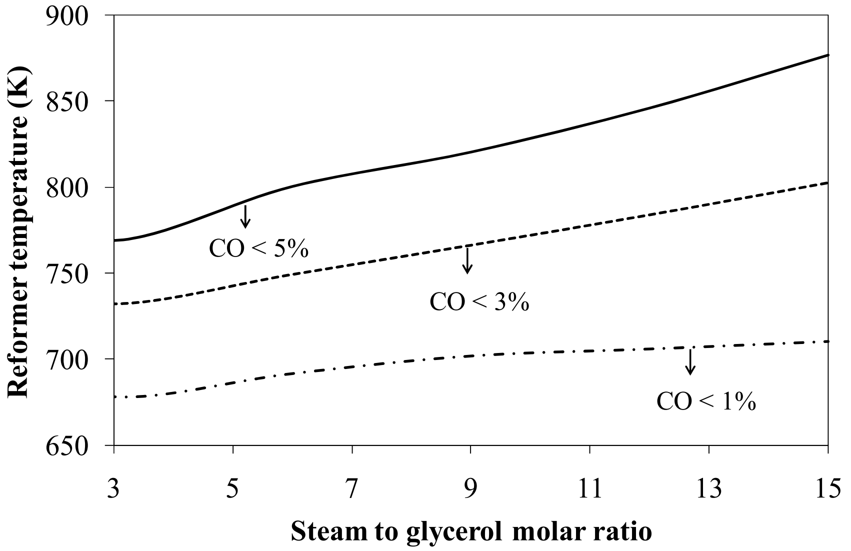


Fig. 1. Operating condition boundary of a glycerol steam reforming for HT-PEMFC.

References

[1]. Zhang J., Xie Z., Zhang J., Tang Y., Song C., Navessin T., Shi Z., Song D., Wang H., Wilkinson D.P., Liu Z. and Holdcroft S. High temperature PEM fuel cells. J. Power Sources **2006**, 160, 872–891.

[2]. Das S.K., Reis A., Berry K.J. Experimental evaluation of CO poisoning on the performance of a high temperature proton exchange membrane fuel cell. J. Power Sources **2009,** 193, 691–698.

Acknowledgements

S. Authayanun would like to thank the Office of the Higher Education Commission, Thailand for supporting by grant fund under the program Strategic Scholarships for Frontier Research Network for the Join Ph.D. Program Thai Doctoral degree for this research. Support from the Thailand Research Fund and Chulalonkorn University is also gratefully acknowledged.

Al, Fe-PILLARED CLAYS IN CATALYTIC DECOLORIZATION OF DYE CONTAINING WATER

Banković P.[1], Milutinović-Nikolić A.[1], Mojović Z.[1], Jović-Jovičić N.[1], Žunić M.[1], Dondur V.[2], Jovanović D.[1]

[1]Institute of Chemistry, Technology and Metallurgy, University of Belgrade,
Department of Catalysis and Chemical Engineering, Njegoševa 12, 11000 Belgrade,
Republic of Serbia, E-mail: predragb@nanosys.ihtm.bg.ac.rs
[2]Faculty of Physical Chemistry, University of Belgrade

Al,Fe-pillared clays (PILCs) have shown good performance in catalytic wet peroxide oxidation (CWPO) of organic pollutants in water. They have predominantly been tested in the degradation of phenol [1]. There are seldom reports on their use in the degradation of other organic pollutants such as toluene [2] and dyes [3]. In this work a series of Al,Fe–PILCs with different Fe^{3+} content was synthesized and characterized. Their catalytic performance was studied in the CWPO of food dye tartrazine used as a model compound. Degree of decolorization of tartrazine containing aqueous solution was monitored in relation to different parameters such as Fe^{3+} content and temperature.

The PILCs were obtained using a common procedure [4] consisting of the following steps: grinding, sieving, Na exchange, intercalation, drying and calcination. Fe^{3+} to (Al^{3+}+Fe^{3+}) molar ratios in the pillaring solutions were 0%, 1%, 5%, 10%, 15% and 20%, and the corresponding materials were denominated Al–PILC, Al,Fe1–PILC, Al,Fe5–PILC, Al,Fe10–PILC, Al,Fe15–PILC and Al,Fe20–PILC, respectively. Phase composition, textural and morphological properties of the starting clay and the synthesized PILCs were determined using X-ray diffraction (Philips PW 1710 X-ray powder diffractometer with a Cu anode), physisorption of nitrogen (Sorptomatic 1990 Thermo Finningen), UV-Vis diffuse reflectance spectrometry (Thermo Evolution 500) and scanning electron microscopy (JSM-646 OLV JEOL). Chemical composition of the PILCs was determined using Spectro Spectroflame M - inductively coupled plasma optical emission spectrometer, together with atomic absorption spectrometer. X-ray diffraction analysis confirmed that the pillaring was successful. Chemical analysis confirmed the incorporation of Al^{3+} and Fe^{3+} species in the PILCs.

Catalytic tests were carried out in a semibatch reactor under stirring and constant temperature maintained by circulation of thermostatic fluid using Julabo MC 4 heating circulator. Initial dye concentration was 50 ppm in the presence of excess of H_2O_2.

Catalytic performance of the catalysts was examined using UV-Vis spectrophotometry. Figures 1 and 2 represent degradation of dye during the course of the reaction. The former shows the influence of Fe^{3+} content at temperature as low as 35°C, and the latter the influence of reaction temperature.

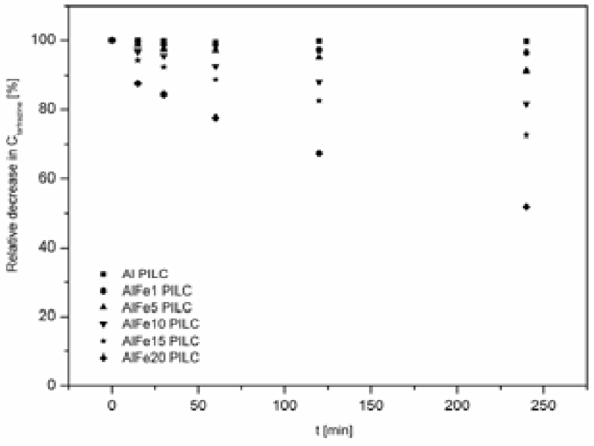


Fig. 1. CWPO of tartrazine on the series of Al,Fe–PILCs at 35°C

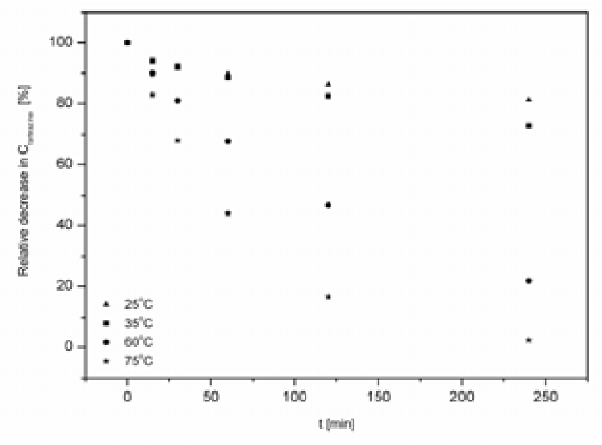


Fig. 2. CWPO of tartrazine on Al,Fe15–PILC at different temperatures

The catalytic tests showed good performance of the obtained Al,Fe–PILCs in the degradation of tartrazine, dependant on the Fe^{3+} content and temperature. For Al,Fe15–PILC it reaches about 98% after 4 h of the reaction conducted at 75 °C. Here investigated method was proven to be efficient in the decolorization of tartrazine containing water, thus reducing sunlight cut-off effects, and have prospects as a first step in a two stage water purification method, where the second one could be biodegradation.

References

[1]. Appl. Clay Sci. **2003** Vol. 22, 303-308.
[2]. Chin. J. Cat. **2009** Vol. 30, 14-18.
[3]. Appl. Catal., B **2009** Vol. 88, 127-134.
[4]. Microporous Mater. **1995** Vol. 5, 97-106.

Acknowledgements

Supported by the Ministry of Science and Technological Development of the Republic of Serbia (Projects 166001 and 142019B).

THIRD GENERATION BIOFUEL PRODUCTION. DESIGN OF CO-IMMOBILIZED LABORATORY PHOTOBIOREACTOR FOR STUDY OF MICROALGAE GROWTH

Barajas A., Kafarov V., Barajas C.

Research Center for the Sustainable Development of Industry and Energy,
Department of Chemical Engineering, Industrial University of Santander,
Bucaramanga, Colombia
Tel +57 7 6344746, e-mail: kafarov@uis.edu.co

According to ChistI (2007). microalgae appear to be the only source of biodiesel (third generation biofuel) that has the potential to completely displace fossil diesel. Unlike other oil crops, microalgae grow extremely rapidly and many are exceedingly rich in oil. Microalgae commonly double their biomass within 24 h. Biomass doubling times during exponential growth are commonly as short as 3.5 h, and their oil content in microalgae can exceed 80% by weight of dry biomass.

The culture of microalgae in photobioreactors is a very complex process, even by coupling the effects of photosynthesis, flow dynamics, mass transfer and irradiance distribution within the reactor (Luo & Al-Dahhan, 2004); but also by the restrictions of the microorganism *per se* such as low metabolism, high salinity tolerance, etc. The production of energy through the system is limited by the efficiency of photosynthesis and cell anabolism (Lehr & Posten, 2009)

The maximization of productivity implies the knowledge of microorganisms response to changes in the physical environment, as an essential step to obtain a cost-effective process. (Schenk et al. 2008)

This work presents the design of a photobioreactor for microalgae production, which optimizes hydrodynamic and mass transfer phenomena, by improving culture mixing owing to the use of static mixers on different angles; in addition, biological phenomena as photosynthesis can also be improved by mixing, which allows a fast movement of cell between dark/light zones inside the reactor, this movement make possible the flashing light effect, which avoid the photoinhibition process and helps the release of O_2 form the reactor. The use of co-immobilizer materials as static mixers, raise the cell productivity by its polymeric nature and prevents the cell adhesion on the reactor walls and allow easier harvesting of the biomass produced.

The results show that the proposed photobioreactor allows the precise study of all types of phenomena involved in microalgae cultivation, and their laboratory-scale optimization permit better understanding of the processes for further scale up to industrial level.

This work was sponsored by the Iberoamerican Science & Technology Development Programme CYTED, the international project 306RTO279 “New technologies for biofuels production” UNESCO codes: 330303, 332205, 530603, 330399, the Colombian Agriculture & Rural Development Ministry, and the Colombian Petroleum Institute ICP-ECOPETROL.

References

[1]. Chisti Y. (2007). Biodiesel from microalgae. Biotechnology Advances 25, 294–306.

[2]. Csogor Z., Herrenbauer M., Perner I., Schmidt K., Posten C. (1999). Design of a photo-bioreactor for modelling purposes. Chemical Engineering and Processing 38: 517–523.

[3]. Lehr F., Posten C. (2009). Closed photo-bioreactors as tools for biofuel production. Curr Opin Biotechnol. 20(3):280-5.

[4]. Luo H., Al-Dahhan M. (2004). Analyzing and Modeling of Photobioreactors by Combining First Principles of Physiology and Hydrodynamics. Biotechnol Bioeng. 85(4):382-93.

[5]. Schenk P., Thomas-Hall S., Stephens E., Marx U., Mussgnug J., Posten C., Kruse O., Hankamer B. (2008). Second Generation Biofuels: High-Efficiency Microalgae for Biodiesel Production. BioEnergy Research. 1(1):. 20-43.

PP-III-7

PREPARATION OF LOCAL CATALYST AND ITS APPLICATION IN PROCESSES FOR CONVERTING HEAVY PETROLEUM FRACTIONS

Ben Tahar N., Mimoun H.

M'Hamed Bougara University Boumerdes Algeria, nbentahardz@yahoo.fr
Université de Boumerdès-Algerie

The solids are widely used in the refining industry. They are involved in most processes of heterogeneous catalysis that has greatly revolutionized the refining processes during the half past century. It has contributed to the rapid development of processes such as: catalytic cracking, catalytic reforming and isomerization. As we know, the heterogeneous catalysis or contact catalysis aims to carry out a transformation of gaseous or liquid reactants by using a solid catalyst. The chemical processing occurs at the interface solid-fluid due to the absorption of reactants in the solid surface. This adsorption involves specific sites that are capable of contracting with the reactants of chemical bonds more or less strong. The adsorbed and formed sorts lead to the desired reaction if the catalyst is well selected, which is Sabatier principle. Thus, the establishment of superficial atoms and ions plays an important role. As a whole, the industrial solid catalyst are the heart of refining process and determine their future as well. More and more, the catalytic processes develop at the expense of thermal processes, and the discovery of new catalysts determines the development of new processes.

The needs of refinery are evolving constantly. More and more oil is processed and transformed into noble products such as: fuels, bases for petro chemistry, and lubricants. The industry of transports plays a leading role in this development, made possible by the steady progress of processes and catalysts as well.

The development of specifications of fuels and heavy fuel is becoming increasing severe as far as environment is concerned.

It is in this context that this work has been conducted. Starting from local materials, mainly "bentonite", solid catalysts have been developed. They are analyzed by physic-chemical methods. These catalysts are used to develop the heavy fractions and the residues of oil by the catalytic processes. This is by obtaining clean petrol(fuel) that respect the environment, and petroleum fractions that are considered as important raw materials for petrochemical, pharmaceutical, and cosmetic synthesis.

References

[1]. P.Wuithier "raffinage et genie chimique tome1 technip Paris 1972.
[2]. Tekhnologui Neft et gaz N°1 Moscou 2007.

DE-NO$_X$ SYSTEM BASED ON H$_2$-SCR CATALYSTS

Bensaid S., **Russo N.**, **Fino D.**[1]

Dipartimento di Scienza dei Materiali e Ingegneria Chimica - Politecnico di Torino,
Corso Duca degli Abruzzi 24, 10129 Turin – ITALY
[1]debora.fino@polito.it

The following after-treatment system is based on the on-board generation of activated species, able to reduce NO$_x$ emissions from diesel engines. H_2 and CO are produced through an auto-thermal reforming (ATR) of post-injected fuel, placed as a by-pass of the close coupled DOC (Diesel Oxidation Catalyst) and DPF (Diesel Particulate Filter), as depicted in **Fig. 1**. The proper inlet composition to the reformer is achieved by the simultaneous control of the exhaust gas flow rate, split from the main flow by means of a plug valve, and the required amount of vaporized diesel, fed to the reformer at the front of the reactor. In fact, an appropriate oxygen to carbon ratio has to be ensured into the reformer to enhance H_2 selectivity, and consequently for fuel penalty minimization. A spark ignition system is placed to eliminate light off issues.

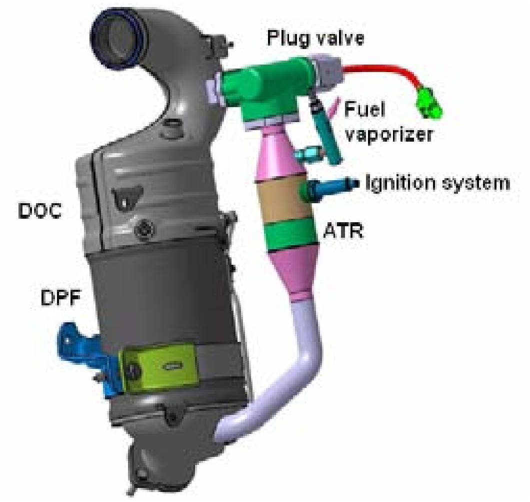


Fig. 1. Prototype of the system.

Some commercial catalysts were tested in order to investigate the performance of the ATR under such conditions. The tests show the reformer performance at different oxygen to carbon ratios and space velocities. The best operating conditions is at a GSHV of 20400 h^{-1}, and an oxygen to carbon ratio equal to 0.5. At each engine operative condition, given an optimal oxygen to carbon ratio in the ATR, and a required H_2 yield for NO$_x$ reduction, fuel consumption can be evaluated, and the exhaust gases split to the ATR is sized accordingly.

A series of perovskite-type catalysts ($LaFeO_3$, $La_{0.8}Sr_{0.2}FeO_3$, $La_{0.8}Sr_{0.2}Fe_{0.9}Pd_{0.1}O_3$, $La_{0.7}Sr_{0.2}Ce_{0.1}FeO_3$, $La_{0.7}Sr_{0.2}Ce_{0.1}Fe_{0.9}Pd_{0.1}O_3$) were prepared by the solution combustion synthesis method and fully characterized by XRD, BET, FESEM and TPD/R analyses. Two of them ($Pd/La_{0.8}Sr_{0.2}FeO_3$, $Pd/La_{0.7}Sr_{0.2}Ce_{0.1}FeO_3$) were prepared by deposition of the Pd nitrate precursor via incipient wetness impregnation onto the pre-formed perovskites. For the sake of brevity, the results of the catalytic activity tests are shown only for $La_{0.7}Sr_{0.2}Ce_{0.1}Fe_{0.9}Pd_{0.1}O_3$, which was selected as the best catalyst on the grounds of temperature programmed reduction (TPR), desorption (TPD), and reaction (TPRe), the latter being the NO to N_2 reduction with H_2, in the absence and in the presence of O_2. The catalyst was then deposited over a cordierite substrate (diameter: 35 mm, length: 25 mm, cell density: 200 cpsi), coated with 5wt% γ-alumina, at a loading W/F equal to 0.02 $g_{cat} \cdot s \cdot cm^{-3}$ (20 wt%). In **Fig. 2-left** it appears that for a NO and H_2 mixture of 1:10 ppmv, without O_2, the catalyst has a T_{50} equal to 130 °C at 30000 h^{-1}, with a complete NO reduction at 200°C. In the presence of O_2 (5 vol%), at least a two-fold higher H_2 concentration was required to achieve the same NO to N_2 reduction obtained with the powder catalyst (**Fig. 2-right**).

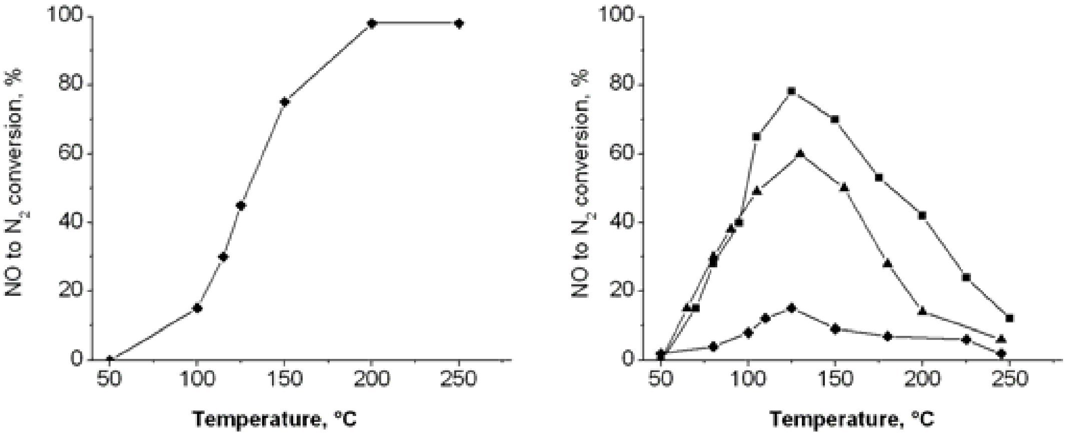


Fig. 2. GSHV = 30,000 h^{-1}. Left: 1,000 ppmv NO, 10,000 ppmv H_2 (♦), N_2 balance;
Right: 100 ppmv NO, 1,000 (♦) – 2,000 (▲) – 4,000 (■) ppmv H_2, 5% O_2, N_2 balance.

As compared to other catalysts of H_2-SCR found in the literature [1-3], the NO_x conversion degree is satisfactory since it is reached without the use of Pt, with a low W/F factor (mass of catalyst over the flow rate), and for temperatures (130°C-150°C) and GHSVs compatible with those of the exhaust line of a diesel passenger car. Studies are now in progress to improve the catalyst selectivity in the presence of O_2, minimizing N_2O and NO_2 porduction for fuel consumption minimization. Hence, presently the fuel penalty is around 4% for a NO_x to N_2 conversion of 60%.

References

[1]. Costa N.C., Savva P.G., Andronikou C., Lambrou P.S., Polychronopoulou K., Belessi V.C., Stathopoulos V.N., Pomonis P.J., Efstathiou, *J. Catal.* **2002**, 209, 456-471.

[2]. Costa N.C, Efstathiou A.M., *Appl. Catal. B*, **2007**, 72, 240-252.

[3]. Ferri D., Forni L., Dekkers M.A.P., Nieuwenhuys B.E. *Appl. Catal. B*, **1998**, 16, 339-345.

Acknowledgements

The EU funded project TOP EXPERT is gratefully acknowledged.

SEPARATION BETWEEN CHLORIDE AND NITRATE ANIONS USING ANION EXCHANGE RESIN IN THE PRESENCE OF POLYETHYLENEIMINE

Berbar Y., Amara M., Kerdjoudj H.

[1]*Laboratoire d'hydrometallurgie et de chimie inorganique moléculaire, Faculté de chimie, USTHB, BP 32, Elalia, Bab ezzouar, Algiers, ALGERIA.*
E-mail: mo_amara@yahoo.fr

Removal of nitrate anion from aqueous solution stays one of the principal goals of much study concerning water treatment. Besides biological and membrane separation treatment, Anion exchange resin technique has been widely investigated and the most result was leading to an efficient elimination. In the proposed work an attempt to the utilization of commercial anion exchange membrane modified by adsorption of polyethyleneimine was investigated. Many conditions of modification of anion exchange resin surface were studied and the influence of the composition of treated solution was also examined. It is observed that the chloride / nitrate ratio has a direct consequence on the separation when modified resin by 2 day adsorption in 2g/L polyethyleneimine solution at pH 10 was used. It is also concluded that increasing of the contact time between resin and polyethyleneimine solution lead to the decreasing of a separation between Cl^- and NO_3^-. Moreover, the conducted study was applied to a real solution provided from underground water in the Sahara at the southern region of Algeria. The separation has been studied in the presence and in the absence of a commercial pesticide commonly used in the region. Obtained result showed that the more concentration of chloride anion the more influence of the pesticide on the fixation process.

PP-III-10

PRODUCTION OF BUTYL ESTERS FROM USED FRYING OIL AND BIOBUTANOL AS A BIODIESEL FUEL

Bouaid A., Hahati K., El boulifi N., Martinez M., Aracil J.*

Chemical Engineering Department, Faculty of Chemistry, University of Complutense
28040 Madrid, Spain. Phone number:+34 91-3944175,
*Fax number: +34 91 394 4167, * E-mail: jam1@quim.ucm.es.*

Abstract

In recent years, there is a great interest in the use of alcohols (ethanol, butanol,.) produced from biomass fermentation as raw materials to produce biodiesel. Fatty acid methyl, ethyl and butyl esters known as biodiesel (ASTM), show large potential applications as diesel substitutes. Butyl esters are the product of transesterification of fats and vegetable oils with Biobutanol in the presence of an acid or an alkaline catalyst.

In the present work, the process of synthesis of butyl esters from used frying oil (UFO) and Biobutanol using KOH as catalyst, has been developed and optimized by application of the Factorial Design and Response Surface Methodology. The effects of temperature and catalyst concentration were studied. Catalyst concentration was found to have the most significant influence on conversion.

The optimum conditions for laboratory scale reactions were found to be a catalyst concentration of 1% and an operation temperature of 90°C with 6:1 Biobutanol/oil molar ratio, obtaining conversion rate of 96.86%. The resulting butyl esters can be used as a diesel fuel substitute, since it matches the European Biodiesel Standard EN 14214.

Producing butyl esters rather than methyl esters is of considerable interest because it allows production of an entirely agricultural fuel and the extra carbon brought by the butanol molecule slightly increases the heat content and the cetane number.

Key words: Alternative fuels, Biodiesel, Used frying oils, Fatty acid butyl esters, Optimization, Response surface methodology.

CONVERSION OF WASTE COTTON TO BIOETHANOL BY MICROWAVE HYDROLYSIS REACTOR

Chen J., Guo J.

Department of Safety, Health and Environmental Engineering,
Hungkuang University, Taichung, Taiwan, R.O.C.
e-mail: jcchen@sunrise.hk.edu.tw.

With issues on the shortage of traditional fossil fuels and global climate change worsening, the development and application of biomass energy has been received increasing attention in many countries. The main raw materials for the bioethanol developed domestically usually come from energy crops that are abundant in starch and saccharide, such as yam, sugarcane, corn, sorghum, and tapioca. Except for these materials, cellulosic biomasses are actually the most abundant source of polysaccharides and extensively exist in various plants such as tree trunk, rice peduncle, grass peduncle, corn peduncle, and sugarcane scraps. After hydrolysis, they convert to reducing saccharides that can be fermented to produce ethanols. Therefore, a great expectation has been put on the study of cellulosic biomass as substitute energy. Many literatures also pointed out use of cellulose to produce ethanol had the most development potential [1-8].

The development of converting cellulosic materials to ethanol started in 1980 [2]. The critical procedure in the process was hydrolysis of cellulose into fermentable saccharide. The crystal structure of cellulose and the tight combination of semi-cellulose, lignin and cellulose posed high difficulty in hydrolysis conversion [5]. The common hydrolytic methods in literatures included acid hydrolysis and enzyme (cellulase) hydrolysis. However, the optimal conditions of these methods were varied with diferent biomass species. The hydrolysis efficiency and reaction rate of these methods were usually poor and slow. It is necessary to develop new method to overcome the bottleneck in the process for cellulose converting to ethanol.

This study uses waste cotton instead of energy crops as biomass raw material and develops innovative microwave hydrolysis technology to improve the hydrolysis rate and conversion efficiency. The waste cotton is washed and dried for one hour at 50°C. After proper cutting and weighing, different hydrolysis reagents, including hydrochloric acid, sulfuric acid, nitric acid and sodium hydroxide, are used to conduct the hydrolysis test. Microwave hydrolysis is performed at substrate concentration of

3%. The filtrate after hydrolysis is subject to analysis for reducing saccharides. The main parameters exammed in the experiments include hydrolysis reagent, acid solution concentration, microwave power, temperature, and reaction time.

Experimental results showed that waste cotton has relatively high cellulose content among all cellulosic biomass but is difficult to be hydrolyzed to reducing saccharides by traditional hydrolysis methods. At room temperature, the hydrolysis efficiency is below 1% for different acid/base reagents and concentrations. With the assist of microwave, the hydrolysis rate and efficiency of waste cotton were significantly increased. Among the various experimental conditions, 30% HCl had the highest hydrolysis efficiency for cotton fiber (38.1%). The next was 37% HCl (34.79%) and 40% H_2SO_4 (27.88%). The optimal microwave temperature and time were 110 °C (power 195W) and 10 min. The increase or decrease in microwave temperature and time lowered the conversion efficiency due to incomplete or over decompostion of cotton fiber. The reducing saccharide obtained from waste cotton by microwave hydrolysis can be fermented with the yeast Saccharomyces cerevisiae and the ethanol yield was 4600 mg/l.

References

[1]. Ballesteros M.; Oliva J.M.; Negro M.J.; Manzanares P.; Ballesteros I. Ethanol from lignocellulosic materials by a simultaneous saccharification and fermentation process (SFS) with Kluyveromyces marxianus CECT 10875. Process Biochemistry **2004**, 39, 1843-1848.

[2]. Dale B.E.; Henk L.L.; Shiang M. Fermentation of lignocellulosic materials treated by ammonia freeze-explosion. Development of Industrial Microbiology **1984**, 26, 223-233.

[3]. Eichhorn S.J.; Baillie C.A.; Zafeiropoulos N.; Mwaikambo L.Y.; Ansell M.P.; Dufresne A.; Entwistle K.M.; Herrera-Franco P.J.; Escamilla G.C.; Groom L.; Hughes M.; Hill C.; Rials T.G.; Wild .M. Review: Current international research into cellulosic fibres and composites. Journal of Material Science **2001**, 36, 2107-2131.

[4]. Saha B.C.; Iten L.B.; Cotta M.A.; Wu Y.V. Dilute acid pretreatment, enzymatic saccharification and fermentation of wheat straw to ethanol. Process Biochemistry **2005**, 40, 3693-3700.

[5]. Iranmahboob J.; Nadim F.; Sharareh M. Optimizing acid-hydrolysis: a critical step for production of ethanol from mixed wood chips. Biomass and Bioenergy **2002**, 22, 401-404.

[6]. Karimi K.; Emtiazi G; Taherzadeh M.J. Ethanol production from dilute-acid pretreated rice straw by simultaneous saccharification and fermentation with Mucor indicus, Rhizopus oryzae, and Saccharomyces cerevisiae. Enzyme and Microbial Technology **2006**, 40, 138-144.

[7]. Kaur P.P.; Arneja J.S.; Singh J. Enzymic hydrolysis of rice straw by crude cellulase from Trichoderma reesei. Bioresource Technology **1998**, 66, 267-269.

[8]. Ohgren K.; Vehmaanpera J.; Siika-Aho M.; Galbe M. High temperature enzymatic prehydrolysis prior to simultaneous saccharification and fermentation of steam pretreated corn stover for ethanol production. Enzyme and Microbial Technology **2007**, 40, 607-613.

Acknowledgements

The authors gratefully acknowledge the National Science Council of R.O.C. (Taiwan) for the financial support.

THE METHOD OF GLYCERIC ACID PREPARATION AND GOLD SUPPORTED CATALYSTS FOR ITS REALIZATION

Čornaja S.[1], **Žižkuna S.**[1], **Muravjova O.**[1], **Kampars V.**[1], **Grabis J.**[2], **Jankoviča D.**[2], **Kampare R.**[1], **Dubencovs K.**[1]

[1]*Riga Technical University, Faculty of Material Science and Applied Chemistry, Riga, Latvia, svetlana@ktf.rtu.lv*
[2]*RTU Institute of Inorganic Chemistry, Riga, Latvia*

Glycerol is the main by-product of biodiesel fuel manufacturing. Glycerol catalytic oxidation by molecular oxygen is one of the feasible methods of glycerol utilization. A number of important and valuable products, which are used as a feedstock in various processes of organic synthesis, can be obtained in the process of glycerol oxidation. Currently the supply of these chemicals is limited due to high costs. Glycerol catalytic oxidation by molecular oxygen can substantially decrease the cost of oxidation products.

Kinetics of glycerol oxidation in presence of various gold based catalysts has been studied in this research. There are new synthesized gold containing catalysts and commercial 1,5% Au/TiO_2 catalyst utilized.

According to the data presented in this research, activity of the new Au/TiO_2 catalyst is dependent on the catalyst specific surface (Scs), gold particles size (dAu), NaOH initial concentration, catalyst concentration and oxidation temperature. Activity of the catalyst increases along with decrease of the size of gold particles and increase of Scs.

Research demonstrated that new gold containing catalysts are active, and yield of glyceric acid in presence of the new catalysts is equal to or higher than in presence of the commercial catalyst.

Glyceric acid is obtained as a main product with high yield and selectivity.

Optimal parameters for the production of glyceric acid in closed thermostated gasometrical equipment in presence of 5% Au/TiO_2 catalyst have been determined: T = 333 K, = 1atm, c0(glycerol) = 0,3 M, c0(NaOH) = 1,5 M, n(glycerol)/n(Au) = 300. The yield of glyceric acid is 68 mol% with 85% selectivity, for oxidation time equal to 120 min.

Optimal parameters for the producing of glyceric acid in barbotage type reactor in presence of 5% Au/TiO_2 catalyst have been determined: T = 333 K, = 1atm, c_0(glycerol) = 0,3 M, c_0(NaOH) = 1,5 M, n(glycerol)/n(Au) = 300. The yield of glyceric acid is 79 mol% with 90% selectivity, oxidation time equal to 420 min.

LOW-TEMPERATURE ABATEMENT OF NITROGEN OXIDES (N_2O, NO_x) FROM THE EFFLUENT GASES IN NITRIC ACID PRODUCTION

Chumachenko V.A., Zenkovets G.A., Shutilov A.A., Kharitonov A.S., Pirutko L.V., Mokrinsky V.V., Noskov A.S.

Boreskov Institute of Catalysis of SB RAS, Pr. Lavrentieva, 5,
Novosibirsk, 630090, Russia, vachum@catalysis.ru

Nitrogen oxides are among the most dangerous air pollutants. Due to highly toxic impact of NO and NO_2 on humans, their emissions are strictly controlled in all basic industries and transport and could be efficiently destroyed by catalytic reduction. Nitrous oxide N_2O is much less toxic, but now it is also considered as an environment pollutant and a greenhouse gas. Industrial large capacity nitric acid (NA) units are one of the greatest sources of both types of nitrogen oxides, contributing some 4-8% of total N_2O emissions. However, in spite of some promising approaches [1-3], the problem of NOx+N_2O abatement has not been entirely solved so far.

In this work we have analyzed the current status of N_2O emissions after NOx catalytic reduction in typical Russian NA technologies and selected the most promising schemes for combined low-temperature NOx+N_2O abatement. Experimental lab-scale testing of new BIC catalysts have shown high activity both in selective catalytic reduction (SCR) of NOx by ammonia, and in subsequent N_2O decomposition.

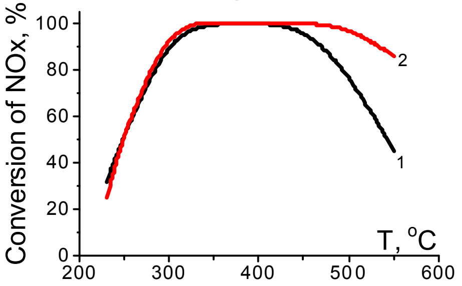
Table 1 N_2O emissions in commercial NA units

NA technology	Method of NOx reduction	N_2O concentration, ppm	
		inlet	outlet
UKL-7	High-temperature, by CH_4 (~700°C)	900-1300	20-50
UKL-7	SCR, by NH_3 (~280-300°C) *	560	780
UKL-7	SCR, by NH_3 (~280-300°C)	900-1200	900-1000
AK-72	High-temperature, by CH_4 (~700°C)	1000-1200	3-50

Concentrations of N_2O in effluent gases upstream and downstream the reactor for NOx reduction are presented in **Table 1**. Systems UKL-7 produce large amounts of N_2O after SCR. Its increase (*) can be caused by improper NH_3 automatic control, or by NH_3 excessive supply under wide variations of NOx content in effluents. So, N_2O abatement in these technological schemes seems quite necessary and reasonable.

Catalytic activity of BIC proprietary and commercial vanadia-alumina catalysts in SCR reaction was studied in a flow reactor at: *GHSV* – 7200 h^{-1}, *[NO]* – 1000 ppm, *[NH_3]* – 1100 ppm, *[O_2]* – 4.5 % vol., *[H_2O]* – 3.0 % vol., *[He]* – balance. Degree of

Fig. 1.



NOx conversion vs. temperature is presented in **Fig. 1**. Here, *1* – commercial catalyst AVK-10 (V_2O_5/Al_2O_3); *2* – new catalyst BIC-1 (V_2O_5-WO_3/TiO_2.

Nanostructured catalyst (2) BIC-1 features by increased thermal stability and mechanical strength. At the same activity, working temperature range of (*2*) is broader than that of (*1*), no N_2O is produced even above stoichiometric ratio NH_3/NO_x, see **Table 2**.

Table 2 Concentration of NO_X and N_2O after SCR in lab-scale reactor

Temperature, °C	250		300		350-400		500-550	
Concentration, ppm	NOx	N_2O	NOx	N_2O	NOx	N_2O	NOx	N_2O
Catalysts								
AVK-10	478	-	41	-	0	2	0-2	23-50
BIC-1	462	-	0	-	0	0	0	2-10

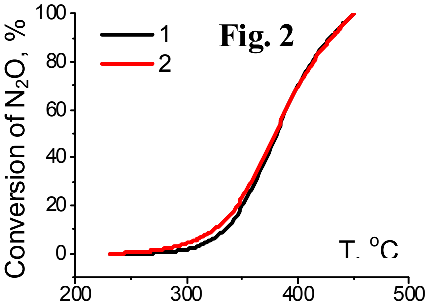
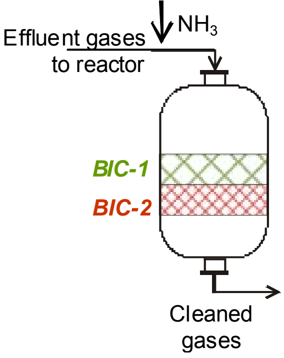


Fig. 2

Activity of zeolite-based catalysts in low-temperature N_2O decomposition was studied at: (*1*) *GHSV* – 7200 h^{-1}, *[NO]* – 1000 ppm, *[N_2O]* – 700 ppm, *[O_2]* – 4.5 % vol., *[H_2O]* – 2.0 % vol., *[He]* – balance; (*2*) added *[NH_3]* – 1100 ppm, see **Fig.2**. Catalyst BIC-2 (Fe/ZSM-5) showed the best activity and stability, conversion of N_2O under 450°C was as high as 97-99%. No significant effect of inlet NH_3 was observed.

Fig. 3



Starting from these preliminary results, we have proposed the combined approach to low-temperature catalytic abatement of NOx+N_2O for UKL-7 in existing reactor, using BIC-1 (or AVK-10) and BIC-2 catalysts, see **Fig.3**. Expected conversion of NOx is 96.5-98%, conversion of N_2O 97-99% at: *GHSV* – 4,200 h^{-1}, inlet temperature 300-350°C, other inlet parameters – close to industrial values.

References

[1]. F.Kapteijn, J.Rodriguez-Mirasol, J.A.Moulijn, *Appl. Catal. B: Environ.*, 1996, vol. 9, is.1-4, pp.25-64.

[2]. M.Kogel, B. Abu-Zied, M.Schwefer, T.Turek, *Catal. Commun.*, 2001, vol.2, is.9, pp.273-276.

[3]. M.Groves, R.Maurer, M.Schwefer, R.Siefert, *Report at:* NITROGEN 2006 Intern. Confer., Vienna, Austria – March 14th, 2006.

COMPARISON OF Pd-BASED MEMBRANES WITH DIFFERENT INTERMEDIATE LAYERS FOR HYDROGEN PRODUCTION

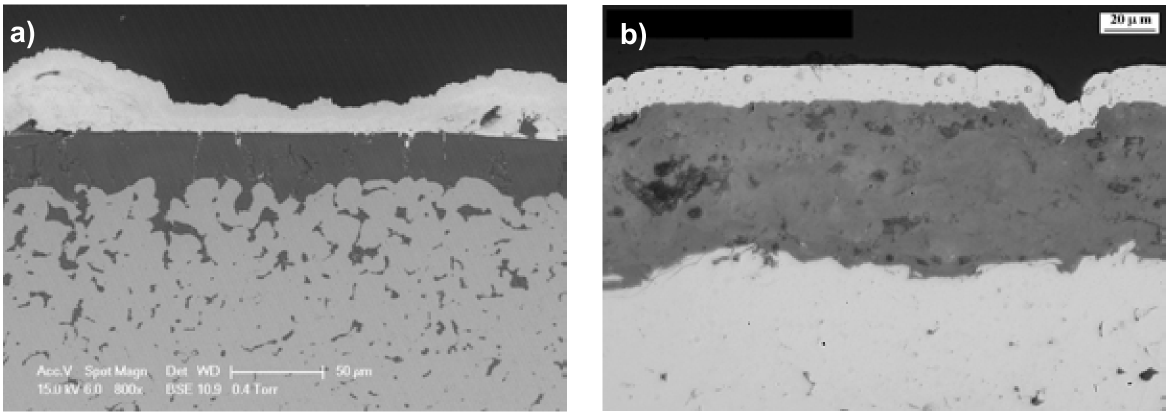
Corengia P.[1], **Fernandez E.**[1], **Calles, J.A.**[2], **Sanz R.**[2], **Alique D.**[2]

[1]*INASMET-Tecnalia*
Mikeletegi Pasealekua 2, 20009 San Sebastián, Donostia, Spain
E-mail: pablo.corengia@inasmet.es
[2]*Department of Chemical and Energy Technology, Universidad Rey Juan Carlosc/*
Tulipán s/n, 28933 Móstoles, Madrid, Spain

Nowadays, the global interest in developing the hydrogen economy is generating an important research activity for optimization hydrogen production processes. In this context, Pd-based membranes represent a suitable alternative for hydrogen separation and membrane reactor applications [1]. Nevertheless, pure Pd membranes present some important drawbacks such as H_2 embrittlement and poisoning by sulfur compounds for its industrial application. These problems can be solved alloying the Pd membrane with other metals, mainly Ag or Cu. Instead of preparing a thick Pd-based foil (high Pd cost and poor permeation properties), an advisable alternative is the production of a Pd-based composite membrane consisting of a thin selective layer (Pd or its alloy) deposited onto a porous support. There is a large variety of techniques for obtaining composite Pd-based membranes over different supports, including electroless plating, electroplating, chemical vapour deposition or physical vapour deposition. Attending the economy of the covering, electroless plating (ELP) is one of the most attractive techniques due to their simplicity, facility for covering complex geometries and ease to scale-up [2]. However, Physical Vapour Deposition (PVD) is less laborious, provides faster deposition rates, allows better control of the film thickness and alloy composition, and also is an eco-friendly dry process [3,4]. In the case of using a metallic support, the deposition of an additional layer is necessary for avoiding the intermetallic diffusion between compounds of the support and Pd-based layer at high temperatures. Tungsten, tungsten oxide, tantalum oxide, iron oxide, aluminium oxide, zirconia, titania, zeolite, and silica were used as an effective diffusion barrier [5].

This study has been focused on the comparison between selective membranes for H_2 separation obtained over modified PSS supports with an intermediate layer by ELP and PVD-Magnetron Sputtering techniques. PSS supports purchased from Mott Metallurgical have been initially cleaned by consecutive washing with HCl, NaOH and ethanol solutions under ultrasonic irradiation at 333 K. After that, an intermetallic diffusion barrier (mainly YSZ or silicalite-1) has been incorporated for avoiding the intermetallic diffusion at high temperatures and reducing both roughness and average pore diameter in surface, by sol-gel and atmospheric plasma spraying techniques. Finally, the incorporation of Pd (or alloys) over modified supports has been carried out by both techniques mentioned above. Pd, Ag and Cu targets have been employed as metal source for PVD while palladium chloride and silver nitrate have been reduced with hydrazine in the ELP. The processing conditions for intermediate layer and selective layer deposition methods have been optimized and the manufactured membranes have been characterized by SEM, EDX, XRD, profilometry, mercury porosimetry and gravimetric analysis.

Moreover, regarding the diffusion barrier layer, the gas permeability reduction has been evaluated. Additionally, gas permeation and separation properties of the prepared membranes have been evaluated for H_2 and N_2 as a function of differential pressure, temperature and time exposure, comparing the effectiveness of ELP and PVD techniques for preparing dense layers. Furthermore, these gas permeation and separation results have been compared with the technical targets set by DOE for 2015 (U.S. Department of Energy) [6].



[redacted]

SEM micrograph (cross-section view) of:
(a) PSS/Silicalite-1/Pd by ELP, (b) PSS/YSZ/Pd by PVD.

References

[1]. Saracco G., Neomagus H., Versteeg G.F., van Swaaij; Chem. Eng. Sci. 54 (1999) 1997.

[2]. Rothenberger K.S., Cugini A.V., Howard B.H., Killmeyer R.P., Ciocco M.V., Morreale B.D., Enick R.M., Bustamante F., Mardilovich I.P., Ma Y.H.; J. Membrane Sci. 244 (2004) 55.

[3]. Klette H.; Bredesen R.; Membrane Technology 2005 (5) (2005) 7.

[4]. Jayaraman V.; Lin Y.S., Pakala M., Lin R.Y. J. Membrane Sci. 99 (1995) 89.

[5]. Samingpraia S.,Tantayanon S.,Ma Y.H. J. Membrane Sci. 347 (2010) 8.

[6]. Hydrogen from Coal R&D Program. Office of Fossil Energy, National Energy Technology Laboratory, U.S. Department of Energy. September 2007. Page 33.

Acknowledgements

The authors are very grateful for the financial assistance granted by the Spanish Ministry for Science and Innovation under the SEPHYCO project.

PP-III-15

PARTIAL OXIDATION OF METHANE TO SYNTHESIS GAS OVER POROUS NICKEL BASED CATALYSTS

Danilova M.M., **Fedorova Z.A., Kirillov V.A., Zaikovskii V.I., Kuzin N.A.,**
Kuzmin V.A., Krieger T.A.

Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
e-mail: Sabirova@catalysis.ru

The catalytic process of the partial oxidation of methane (POM) to synthesis gas is now considered as a promising way for producing synthesis gas. POM is accompanied by the deep CH_4 oxidation to CO_2 and H_2O with a considerable heat release. The use of heat-conducting catalysts will aid in diminishing the temperature gradients, local overheatings, and sintering of the active component. To afford high conductivity of the catalysts, it is reasonable to use the metallic supports. In this work, we studied the catalytic properties of the nickel catalysts supported on porous nickel with MgO precoat in the reaction of POM to the synthesis gas and also tested the developed catalysts in reactor of partial oxidation of methane to synthesis gas for solid oxide fuel cell.

The developed catalysts contained 5 wt.% MgO and 3-5 wt.% Ni supported on porous nickel. The catalysts were characterized by XRD, low-temperature adsorption of nitrogen, SEM and TEMHR in combination with EDX analysis. Catalytic activity in the POM was determined by a flow method (quartz reactor, 1 atm, 800°C, natural gas-22 vol.%, air-78 vol.%, $O_2/C = 0{,}65$, feed rate of the reaction mixture - 51,0 l/h, $m_{cat}=0{,}40$ g). Prior to testing the catalysts were reduced at 800-900°C for 1 hour in H_2 flow.

Figure 1 shows the effect of duration of the POM reaction (100 h) on the CH_4 conversion and the selectivity for CO and H_2 on supported nickel catalysts. The CH_4 conversion decreased by no more than 15-25 rel. %. The selectivity for CO and H_2 showed a slightly decrease. The most stable activity was observed for the sample reduced at 900°C.

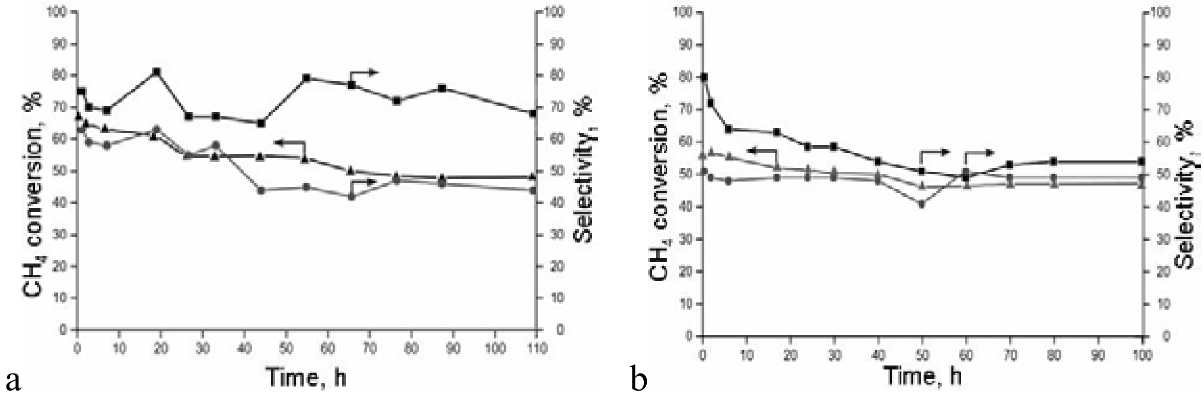


Fig. 1. CH_4 conversion (▲) and selectivity for CO (■) and H_2 (●) versus time on stream in the POM over catalyst 3.0 % Ni/rpNi + 5.0 % MgO, reduced in H_2: a - at 800°C, b – at 900°C.

The conversion of O_2 was 98-99 % and didn′t substantially decrease with reaction time. The obtained results reveal that the catalysts undergo structural-morphological changes during the POM reaction (100 h). However, a part of supported nickel remains in a stable state as dispersed metallic crystallites (3-10 nm) epitaxially bound with MgO; these crystallites don′t sinter into large aggregates, don′t oxidize, and don′t pass into the $Ni_xMg_{1-x}O$ solid solution. The presence of these crystallites determines perhaps stable performance of the catalysts.

According to TEM data no carbon is detected in the samples after testing.

Developed nickel catalyst was used to prepare a cylindrical axial monolith consisting of alternating flat and corrugated ribbons (corrugation height 2 mm, monolith diameter 36 mm and height 54 mm). According to the test data (flow reactor, autothermal regime, 23 vol % of natural gas in air, τ = 0.15–0.04 s, T_{in} = 829-1023°C, T_{out} = 732-941°C) the monolithic catalyst provides the CH_4 conversion not lower than 90 %, S_{CO} – 82-88 %, S_{H2} – 82-97 % and syngas yield 41–48 %.

Resource testing of structured porous nickel based catalyst was perfomed in reactor of partial oxidation of methane to syngas for solid oxide fuel cell (23 vol % of natural gas in air, τ = 0.25 s, T = 800-850°C, Vcat = 165 cm^3). It was shown that concentrations of H_2 and CO were almost constant during the 1000 h testing (Fig. 2), the concentration of methane at the outlet from the reactor didn′t exceeded 0,1 %. Product composition was close to equilibrium.

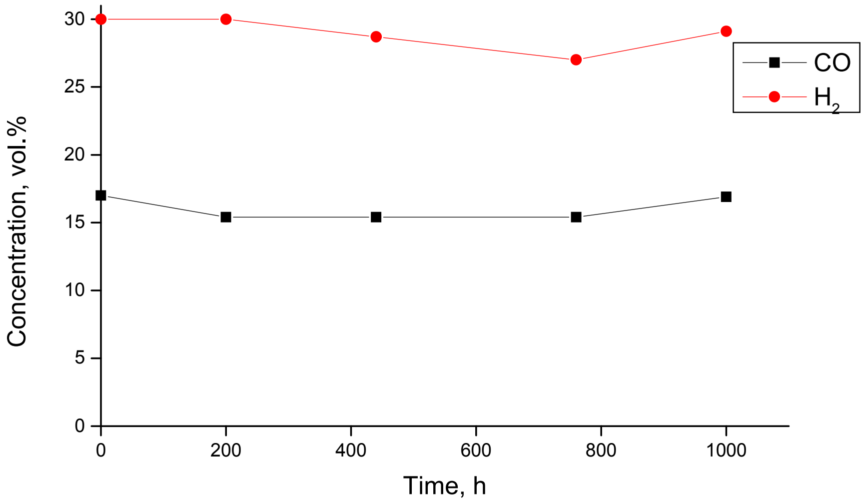


Fig. 2. H_2 and CO concentrations at the outlet from the reactor of partial oxidation of methane to syngas for solid oxide fuel cell versus time on stream.

Thus, the developed nickel catalysts supported on the ribbon porous nickel with MgO precoat are active and stable in the partial oxidation of natural gas.

PP-III-16

INFLUENCE OF MOLYBDENUM ON THE STABILITY OF IRON OXIDE MATERIALS FOR CO FREE HYDROGEN PRODUCTION VIA CYCLIC WATER GAS SHIFT PROCESS

Datta P.[1], **Rihko-Struckmann L.K.**[1], **Sundmacher K.**[1,2]

[1]*Max Planck Institute for Dynamics of Complex Technical Systems,*
Magdeburg, Germany, E-mail: datta@mpi-magdeburg.mpg.de,
[2]*Otto-von-Guericke University, Magdeburg, Germany*

A low temperature fuel cell, e.g. a polymer electrolyte fuel cell (PEFC) does not tolerate high concentrations of carbon monoxide (CO) without significant power loss. Therefore, the removal of CO down to 10-50 ppm in a biomass gasification gas is necessary if the product gas is used in PEFC. This is conventionally done by high and low temperature water gas shift reactors followed by a selective oxidation unit. Recently, another approach has been suggested, where the CO content has been reduced in a single reactor, namely by a cyclic water gas shift reaction unit (CWGS) which is based on the periodic reduction and re-oxidation step of Fe_2O_3-$Ce_{0.5}Zr_{0.5}O_2$ [1]. The modified iron oxide is an oxygen storage material which can be used for hydrogen purification. However, such material looses its activity due sintering during repeated reduction and re-oxidation cycles. In order to exploit the full potential of the material one has to mitigate the sintering of Fe_2O_3-$Ce_{0.5}Zr_{0.5}O_2$. Our approach in this contribution is to add a promoter to the material to stabilize it without compromising the oxygen exchange capacity. 80 wt % Fe_2O_3 with 20 wt % $Ce_{0.5}Zr_{0.5}O_2$ was prepared by urea hydrolysis method [2]. Molybdenum as an additional promoter was impregnated into the solid oxide mixture with final elementary Mo content of 1-5 wt%. The chemical composition and the crystalline phase purity were determined by inductively coupled plasma-optical emission spectrometer (ICP-OES) and X-ray diffraction (XRD) respectively. XRD peaks showed the characteristics of Fe_2O_3 and the cubic structure of a ceria-zirconia solid solution. The absence of Mo peaks suggests that it exists either as very small crystallites or as a very thin two dimensional film which will not be detected by XRD. However, the presence of Mo was confirmed by the chemical elementary analysis through ICP-OES. Furthermore, reproducibility of the synthesis was checked by the chemical analysis which revealed that the expected amount of Fe, Ce, Zr and Mo existed in the samples. The samples were further characterized by BET surface area, thermo gravimetric analysis (TGA), temperature programmed reduction (TPR), X-ray photo electron spectroscopy (XPS)

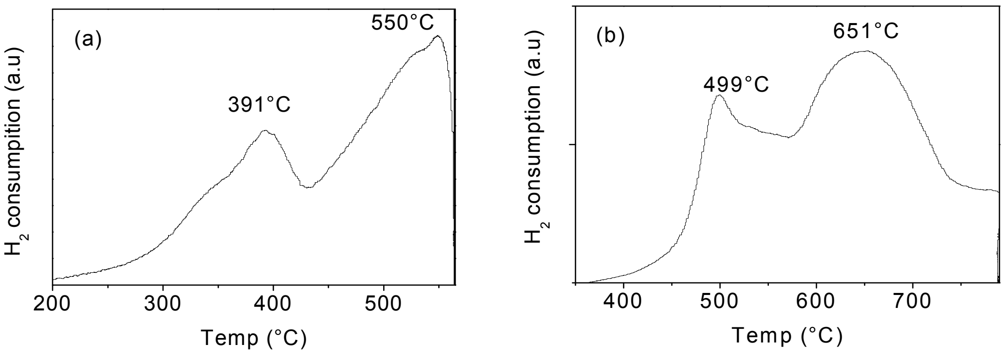


Fig. 1: Experimental H_2-TPR data for (a) Fe_2O_3-$Ce_{0.5}Zr_{0.5}O_2$ and (b) Fe_2O_3-$Ce_{0.5}Zr_{0.5}O_2$ with 2 % Mo promoter.

Scanning electron microscopy (SEM) and by the Fourier Transform Infrared spectroscopy (FT-IR). TPR results (Fig. 1) suggest that the addition of Mo shifted significantly the reduction temperature of Fe^{3+} to magnetite from 391°C to 499°C and the further reduction temperature peak from 550°C to 650°C. This observation indicates that Mo hinder the formation of metallic iron increasing the active phase stability. The assignment of the reduction peaks to the individual mechanistic step is not straightforward in a mixed oxide like Fe_2O_3-$Ce_{0.5}Zr_{0.5}O_2$ as reduction of Fe_2O_3 as well $Ce_{0.5}Zr_{0.5}O_2$ by hydrogen is a two step process with considerable overlapping [3]. Activity measurements were carried out at atmospheric pressure in a quartz tube microreactor at temperatures between 600°C and 750 °C. The iron oxides were reduced by H_2 and oxidized by steam with helium as carrier gas. It was found that Mo improves the stability of $80Fe_2O_3$-$20Ce_{0.5}Zr_{0.5}O_2$ [Fig.2]. A sample modified with 5 % Mo when tested for 100 redox cycles, maintain its activity nearly unchanged at 650°C and retains 90 % of its activity at 750°C whereas the amount of produced hydrogen progressively decreases for the unmodified samples. The results indicate that Mo is successful in hindering the sintering.

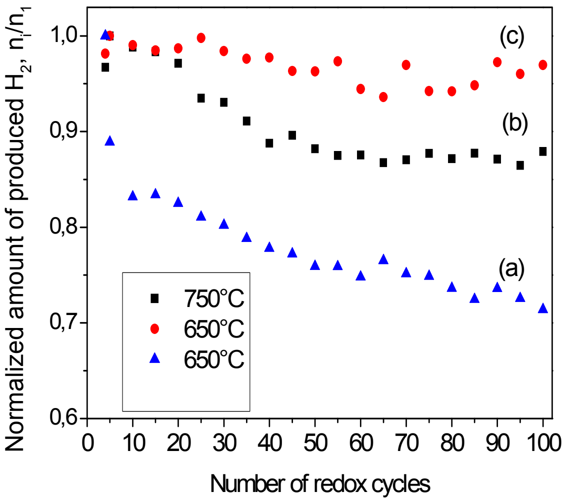


Fig. 2: Variation of normalized amount of produced H_2 with redox cycles at various temperatures for (a) Fe_2O_3-$Ce_{0.5}Zr_{0.5}O_2$, (b) Fe_2O_3-$Ce_{0.5}Zr_{0.5}O_2$ with 5 % Mo and (c) Fe_2O_3-$Ce_{0.5}Zr_{0.5}O_2$ with 5 % Mo.

References

[1]. Galvita and Sundmacher, Chem. Eng. J., 134 (2007), 168-174.
[2]. Galvita et al., Ind. Eng. Chem. Res., 47 (2008), 303-310.
[3]. Galvita et al., J. Mater. Sc., 42 (2007), 9300-9307.

PP-III-17

ETHYLENE FROM ETHANOL OVER HETEROPOLYACID INCORPORATED MESOPOROUS CATALYSTS

Dogu T.[1], Ciftci A.[1], Tokay K.C.[1], Varisli D.[2], Dogu G.[3]

[1]*Middle East Technical Univ., Chem. Eng. Dept. Ankara Turkey, tdogu@metu.edu.trl*
[2]*Gazi University, Institute of Sciences, Ankara Turkey*
[3]*Gazi University, Chem. Eng. Dept. Ankara, Turkey*

Production of petrochemicals [1-3] from a non-petroleum feedstock has attracted significant attention of researchers in recent years. Ethylene and diethylether can be produced by dehydration of ethanol over solid acid catalysts [3,4]. Discovery of ordered mesoporous silicate structured materials [5] started a new research area in catalysis. Heteroplyacids (HPA) are known to have very strong Bronsted acidity and tested as catalysts in number of acid catalyzed reactions. Major disadvantages of these materials are their very low surface area and high solubility in polar solvents, which limit their catalytic applications. In the present study, tungstophosphoric acid (TPA) incorporated mesoporous silicate structured catalysts were synthesized following a one-pot hydrothermal procedure and their ethanol dehydration activities were compared with the silicotungstic acid (STA) incorporated mesoporous catalysts prepared in our recent work [6].

Experimental

Heteroplyacid (HPA) incorporated silicate structured mesoporous catalysts were synthesized following a direct hydrothermal procedure using TEOS and cetyltrimethylammonium bromide as the silica source and the surfactant, respectively. TPA or STA was added to the synthesis solution and hydrothermal synthesis was achieved in a Teflon lined autoclave. The synthesized material was then throughly washed and calcined for the removal of surfactant. Calcination temperature was decided from the thermal analysis of the raw materials and FTIR analysis of the calcined products. Activities of the synthesized materials were tested for ethanol dehydration in a vapor phase flow reactor. Details of the experimental setup were reported elswhere [3-4].

Results and Discussions

XRD analysis indicated well dispersion of HPA within the amorphous silicate lattice of the mesoporous material. EDS and FTIR analysis indicated well incorporation of TPA or STA into the structure of the catalyst and mild distortion of the characteristic structure of the heteropolyacid during the synthesis. DRIFTS studies of pyridine adsorbed materials showed the presence of strong Bronsted acid sites in these catalysts. The synthesized materials were quite stable and the incorporated HPA did not dissolve in water during the washing steps of the material. Nitrogen adsorption analysis indicated Type IV isotherms, indicating mesoporous structure, and gave BET surface area values in the range of 180-250 m^2/g. Activity comparison of TPA and STA incorporated materials (TPA-75(L) and TRC-75(L), respectively) showed higher activity of STA incorporated material (Fig.1) in ethanol dehydration. A decrease of diethyl ether selectivity and a corresponding increase in ethylene selectivity was observed with an increase in temperature (Fig.2) Very high conversion and ethylene selectivity values (approaching to 100%) at temnperatures of 300-400°C were highly promising. Considering that both of these materials were synthesized with a synthesis solution containing a W/Si ratio of 0.4, higher activity of STA incorporated material was considered to be due to higher number of protons of STA and its higher stability in keeping its Bronsted acidity during calcination.

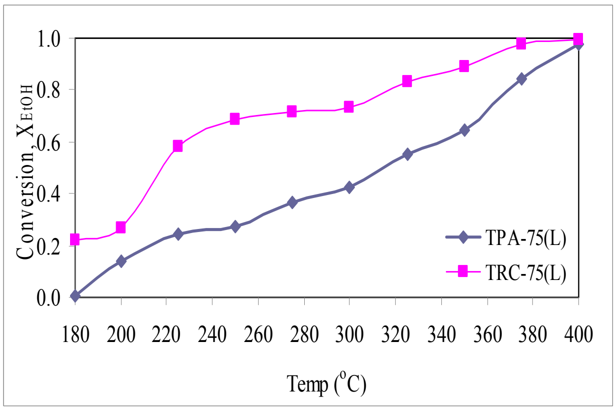


Fig. 1. Ethanol conversion

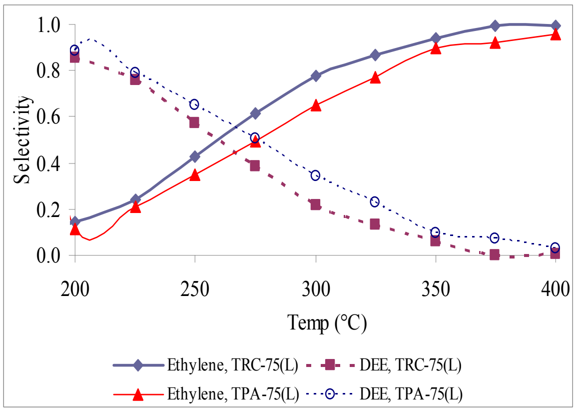


Fig. 2. Ethylene and DEE selectivities.

References

[1]. Pereira C.J. “New Avenues in Ethylene Synthesis”, Science, **1999**, 285, 670-671.

[2]. Dogu T., Varisli D., Alcohols as Alternatives to Petroleum for Environmentally Clean Fuels and Petrochemicals”, Turk. J. Chem., **2007,** 31, 551-567.

[3]. Varisli D., Dogu G., Dogu T., “Petrochemicals from Ethanol over a W-Si-based Nanocomposite Bidisperse Solid Acid Catalyst”, Chem. Eng. Sci., “Petrochemicald from Ethanol over a W-Si-based Nanocomposite Bidisperse Solid Acid Catalyst”, **2010,** Chem. Eng. Sci., 65, 153-159.

[4]. Varisli D., Dogu T., Dogu G., “Novel Mesoporous Nanocomposite WO$_x$-Silicate Acidic Catalysts: Ethylene and Diethyl ether from Ethanol”, Ind. Eng. Chem. Res., 48, 9394-9401, 2009.

[5]. Kresge C.T., Leonowicz M.E., Roth W.J., Vartuli J.C., Beck J.S., “A New Family of Mesoporous Molecular Sieves”, Nature, **1992**, 359, 710.

[6]. Ciftci A., Varisli D., Dogu, T., “Dimethyl Ether Synthesis over Novel Silicotungstic Acid Incorporated Nanostructured Catalysts”, Int. J. Chem. Reactor Eng., **2010,** in press.

Acknowledgements TUBITAK Grant, METU and Gazi University Research Funds.

PP-III-18

SUPPORT INFLUENCE ON Ni-BASED CATALYSTS FOR HYDRODEOXYGENATION REACTION OF BIOFUEL-PRECURSORS

Echeandia S.[1], **Barrio V.L.**[1], **Cambra J.F.**[1], **Arias P.L.**[1], **Güemez M.B.**[1],
Khromova S.A.[2], **Yakovlev V.**[2]

[1]*School of Engineering (UPV/EHU), c/ Alameda Urquijo s/n, 48013 Bilbao (Spain)*
jose.cambra@ehu.es
[2]*Boreskov Institute of Catalysis SB RAS, Pr. Akad. Lavrentieva, 5, Novosibirsk, Russia*

Introduction

Biomass is a renewable alternative to fossil raw materials for the production of liquid fuels and chemicals. Pyrolized biomass liquid fractions contain oxygenated molecules that must be removed to improve the stability of these liquid fuel precursors. A hydrotreating process, hydrodeoxygenation (HDO), is commonly used for this purpose [1]. Therefore study of their deoxygenation is a subject of interest.

Phenol HDO is generally accepted to proceed via two parallel reaction pathways [2]: O-C bond cleavage giving aromatic products (direct hydrogenolysis), or aromatic ring hydrogenation before O-C bond cleavage (combined hydrogenation-hydrogenolysis). In the latter route, alicyclic products are formed and the corresponding alicyclic alcohols appear as short-lived intermediates [3]. The influence of catalyst formulations and activations on those two HDO mechanisms will be fully discussed. The phenol, as a model compound, is used in order to screen different hydrotreating catalysts in HDO. The supports studied are: Al_2O_3, CeO_2, ZrO_2, ZrO_2-CeO_2.

Experimental & Results and discussion

Activity tests were carried out in a bench-scale fixed-bed catalytic reactor with 0.2 g of catalysts. Hydrogen and liquid feed were fed to the reactor in a molar ratio of 100:1 in H_2 : phenol. The experimental conditions were as follows: temperature in the range 423-573 K, total pressure of 1.5 MPa and space velocity of 0.5 $g_{phenol}/g_{catalyst}\cdot h$ corresponding to a model feed consisting of 1 wt% phenol and n-octane as solvent. The liquid products were analyzed by off-line MSD for identification and FID for quantification.

Steady-state conversion data for phenol HDO over reduced Ni-based catalysts are represented in Figure 1. These data are the average of conversion archived during 6 h of time on-stream. During this time the phenol conversion changes were < 3 %. As it can be seen in the Figure 2, in which phenol conversion is represented, nearly total phenol conversion was reached and none or little deactivation seems to have been occurred, except in the case of the alumina-supported catalysts that present a drop of approximately 6%.

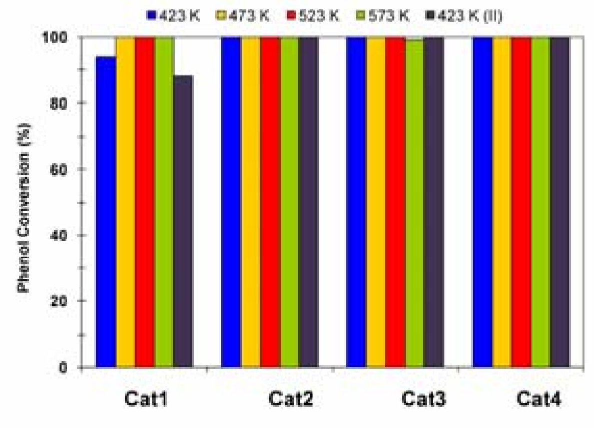


Figure 1. Influence of temperature on phenol conversion with Ni-based catalysts.

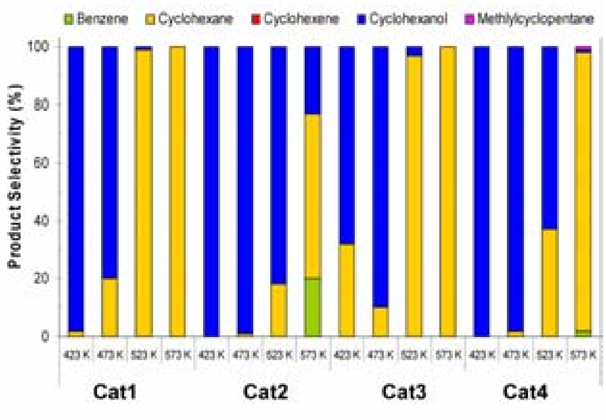


Figure 2. Influence of temperature on products selectivity with Ni-based catalysts.

For the catalysts studied the products with the highest selectivity was cyclohexanol at low temperatures and cyclohexane at high temperatures (Figure 2). The most important products were cyclohexanol, cyclohexane and benzene. This fact indicates a unique reaction pathway in the HDO of the phenol, which is the hydrogenation-hydrogenolysis. First hydrogenation took place converting phenol into cyclohexanol, especially at low temperatures. Then, hydrogenolysis occurred through the breakage of the oxygen-carbon bond and finally a subsequent hydrogenation converted the cyclohexanol into cyclohexane. It is noteworthy that at high temperature (573 K) and a WHSV of 0.5 h^{-1}, in the catalysts supported with ceria showed the direct hydrogenolysis contribution started and benzene as product appeared. Also at the highest temperature methylcyclopentane was also formed from cyclohexane isomerization.

Conclusions

The main conclusions of this research are: i) Ni-based catalysts are very promising in biomass derived liquids HDO; ii) for the Ni-based catalysts the phenol conversion is very high and it seems that the preference route of reactions is the hydrogenation-hydrogenolysis; iii) with these catalytic systems alicyclic products are formed and the corresponding alicyclic alcohols appear as short-lived intermediates specially at low temperatures; iv) the stability in these catalysts seems to be quiet high although a small deactivation was found where Al_2O_3 was used as support.

References

[1]. E. Furimsky, Appl. Catal., A 199 (2000), 147-190.

[2]. Viljava T.R., Doctoral Thesis, Helsinki University of Technology, Espoo, Finland, 2001.

[3]. I. Gandarias, V.L. Barrio, J. Requies, P.L. Arias, J.F. Cambra, M.B. Güemez. Int. J. Hydrogen Energy 33(13) (2008) 3485-3488.

Acknowledgements

The authors thank financial support from the MICINN (project HIREUS) and the Basque Autonomous Government.

STEAM, DRY AND DRY-STEAM REFORMING OF METHANE TO SYNTHESIS GAS ON POROUS NICKEL BASED CATALYSTS

Fedorova Z.A., Danilova M.M., Kirillov V.A., Zaikovskii V.I., Kuzin N.A.,
Krieger T.A., Kuzmin V.A.

Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia,
e-mail: Sabirova@catalysis.ru

CH_4 and CO_2 are the base biogas components and their conversion leads to the syngas production. For carrying out the endothermic reactions of steam, dry or dry-steam reforming of CH_4, intensive heat transfer to the reaction zone is required. Therefore, the catalyst must have a high thermal conductivity. It is most promising to use catalyst on metallic supports. This work was aimed to the developing of the nickel catalysts supported on the porous nickel for CH_4 conversion to syngas, studying their catalytic properties in the reactions of H_2O, CO_2 and mixed H_2O-CO_2 reforming of CH_4 in the constructed pilot reactor.

The developed catalysts contained 5-10 wt.% MgO and 3-8 wt.% Ni supported on porous nickel obtained by rolling (S_{sp}~0.15 m^2/g, V_Σ~0,1 cm^3/g, r_{preval}~5-60 μm). The catalysts were characterized by XRD, low-temperature adsorption of nitrogen, SEM and TEM HR in combination with EDX analysis.

Catalytic activity in H_2O, CO_2 or mixed H_2O-CO_2 reforming of CH_4 was determined by a flow method (750°C, 1 atm, CH_4:H_2O = 1:2 or CH_4:CO_2:N_2 = 1:1:0,86 and CH_4:H_2O:CO_2 = 1:1.54:0.85, initial mixture flow rate – 25 l/h). The catalytic activity in the steam reforming of CH_4 was additionally determined by a flow-circulation method (750°C, 1 atm, H_2O/CH_4=2.0, initial mixture flow rate - 11,8 l/h). Prior to the testing the catalysts were reduced at 750°C in H_2 flow during 1 h.

The activity of the initial nickel support was low (Table 1, fig.2). Supporting nickel on the MgO underlayer considerably increases catalyst activity in the reactions. Fig.1 shows the effect of duration H_2O and CO_2-H_2O reforming on CH_4 conversion on nickel catalysts.

Table 1. Catalytic activity of nickel supported catalysts in the steam reforming of CH_4
(flow-circulation method, 750°C, 1 atm, H_2O/CH_4 = 2, m_{cat} = 0,80g)

Catalyst	CH_4 conversion, %	k, $cm^3/g_{cat}\times s\times atm$
rpNi (0,1 mm)	9	4
4,6 % Ni/rpNi + 6 % MgO (0,1 mm)	73	11
6 % Ni/rpNi + 6,3 % MgO (0,1 mm)	85	23
5.0 % Ni/pNi+5.0 % MgO (1 mm)	70	9.6
7.8 % Ni/pNi +5.0 % MgO (1 mm)	72	10.6
NIAP-18 (fraction 0,25-0,50 mm)	74	9.4

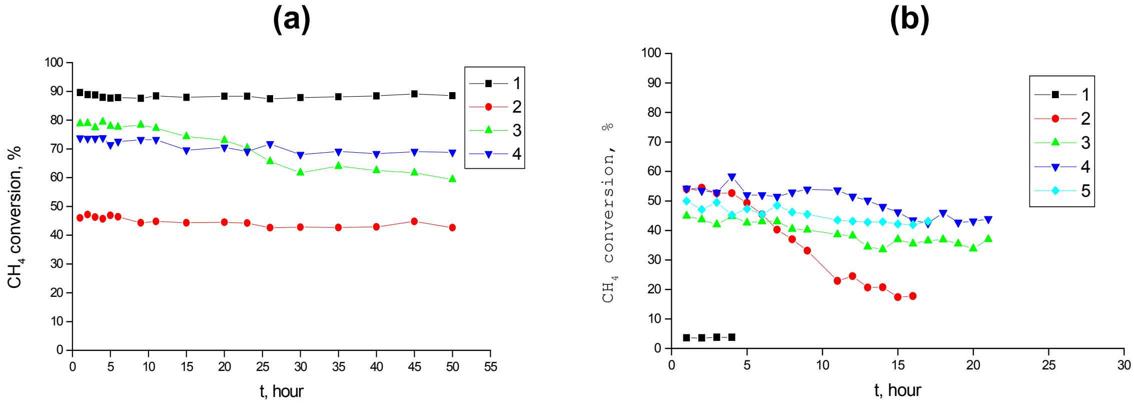


Fig.1 Methane conversion versus time on stream: **a** – steam reforming of CH_4:
1 – 5 % Ni/pNi + 5 % MgO (m=0,80g), 2 – 5 % Ni/pNi + 5 % MgO (m=0,40g),
3 – 2,7 % Ni/rpNi + 6 % MgO (m=0,40g), 4 – NIAP-18 (fraction 0,25-0,50 mm, m=0,80g);
b – dry-steam reforming of CH_4 (m_{cat}=0,40g): 1 – rpNi, 2 - rpNi + 10% MgO,
3 – 2 % Ni/rpNi + 10 % MgO, 4 – 4 % Ni/rpNi + 10 % MgO, 5 – NIAP-18
(fraction 0,25-0,50 mm, m=0,40g).

According to TEM data, fine nickel crystallites (2-5 nm) were appeared in the supported catalysts tested in CH_4 reforming reactions. In agree with XRD data catalysts do not contain the solid solution phase. No carbon deposition were observed by TEM in tested samples.

Special experimental pilot reactor was constructed for testing the developed catalytic monolith (V=41,4 cm^3) based on catalyst 5 wt.% Ni/rpNi + 5 wt.%. MgO. Pilot reactor consisted from three sections located one after another in the developed construction: gas burner (i.d. 100 mm) for combustion of CH_4-air mixture, catalytic reactor (110×30 mm) and evaporater-heat-exchanger (20×90×70 mm). The experimental values of CH_4 conversion and product compositions over developed catalytic monolith in H_2O, CO_2 and mixed H_2O-CO_2 reforming of CH_4 were close to equilibrium values (Table 2).

Table 2. Catalytic activity of catalytic monolith based on porous nickel in steam-, dry- and steam-dry conversion of methane/

Flow rate, l/min			τ, s	Catalyst temperature, °C			Product composition, %				Conversion of CH_4, %	
CH_4	H_2O	CO_2		T_1	T_2	T_3	CH_4	CO_2	CO	H_2		
3,0	3,94	-	0,36	699	745	867	1,2	5,3	21,3	75,2	95,7	experimental value
							0,76	2,1	22,2	75,0	97,0	equilibrium value
3,0	-	3,49	0,38	665	716	799	2,4	5,1	48,3	44,2	90,6	experimental value
							1,1	2,8	50,4	45,6	95,3	equilibrium value
3,0	3,53	1,95	0,29	657	697	806	1,4	7,9	31,8	58,9	94,4	experimental value
							0,27	7,0	31,5	61,3	98,9	equilibrium value

Temperature: T_1 – inlet, T_2 –15 mm after inlet, T_3 – outlet.

Thus, we can conclude that developed catalytic monolith have good activity in H_2O, CO_2 and mixed H_2O-CO_2 reforming of CH_4.

PHASE BEHAVIOR OF ORIENTABLE DIMERS ADSORBED ON SURFACES WITH DIFFERENT GEOMETRY

Fefelov V.F.[1], **Gorbunov V.A.**[1], **Myshlyavtsev A.V.**[1,2], **Myshlyavtseva M.D.**[1]

[1]*Omsk State Technical University, Omsk, Russia*
[2]*Institute of Hydrocarbons Processing SB RAS, Omsk, Russia*
Fefelov_Vasiliy@mail.ru

Adsorption of gases on solid surfaces is an important problem in physical chemistry and chemical engineering [1]. Works belonging to this topic are based on Langmuir's model of adsorption, where adsorbed molecule occupies one adsorption site of surface. However the most of adsorbates are polyatomic molecules and theirs size can significantly exceed size of adsorption site therefore multisite-occupancy theory must be considered. Moreover polyatomic molecules usually don't have spherical symmetry and can have different orientation in adsorbed monolayer with respect to the interface [2]. It leads to absolutely different statistic from one of Langmuir's model [3,4]. It is convenient to investigate such systems through model of dimer adsorption, because dimer is the simplest model of adsorbate which has all required properties (multisite adsorption, horizontal and vertical orientation with respect to interface). Adsorption of dimers actively has been used in last decade [5], but the most of theoretical works, with few exceptions, don't take into account possibility of different orientations of adsorbed dimer with respect to the interface. The aim of present work is study of phase behavior of orientable dimers adsorbed on square, triangular and honeycomb lattices.

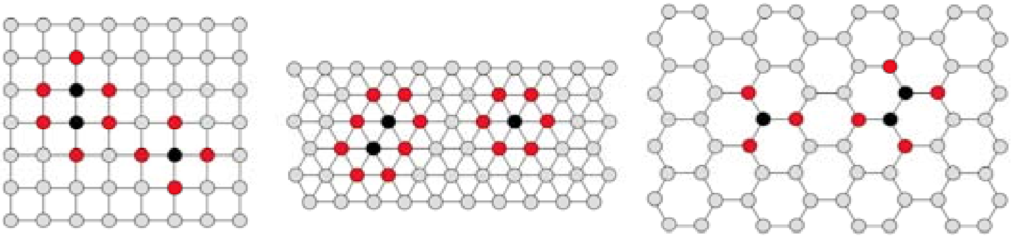


Fig. 1. Types of lattices (square, triangular, honeycomb) and dimers adsorbed on one and two sites (black circles), prohibited for adsorption sites due to infinity strong repulsive interactions (red circles).

To construct the model we used lattice gas (LG) model. In the framework of LG model surface is represented as array of M=L×L adsorption sites in square, triangular or honeycomb arrangement (Fig.1), where L is linear size of the array. As a model of molecule-adsorbate we use dimer composed of 2 identical units with constant bond length equal to the lattice constant. Dimer is the simplest adsorbate, which hasn't spherical symmetry and can adsorb occupying one or two lattice sites (Fig.1). To take into account own size of molecules and its chemical structure we involve infinity strong repulsive interactions between adsorbed nearest-neighbor dimers. Adsorption process is simulated through a grand canonical ensemble. Parameters of the model are temperature, chemical potential, value of difference between adsorption heat on two site of adsorption and one site, size and type of lattice. Model has been investigated with the Monte Carlo method and the transfer-matrix technique.

We have plotted isotherms and coverage curves for all types of lattices, on which one could see well defined plateaus. These plateaus correspond to ordered phases appeared in the system (there are phases consisting of only dimers adsorbed on one site, only two sites and complex structures with both types of adsorbed dimers). For each ordered structure unique order parameter is defined, which is equal to 1 if corresponded phase takes place in the system and equal to 0 otherwise. We have calculated different thermodynamic quantities such as entropy, differential heat of adsorption, adsorption energy etc. Phase diagrams have been plotted for each type of lattices. Fig. 2 shows phase diagram of dimers on square lattice.

From obtained data we conclude that surface geometry has significant influence on ordered phase in similar systems. It is interesting that complex structures, formed by both vertical and horizontal oriented dimers, appear only on triangular and honeycomb lattices, but not on square one. In addition phenomenon of nonmonotonic changing of coverage takes place in our system (only on triangular and honeycomb lattices). It means when pressure in the gas phase growths the amount of empty adsorption sites growths too. We can suppose that all these observed features of dimer adlayer are inherent in real adsorption systems.

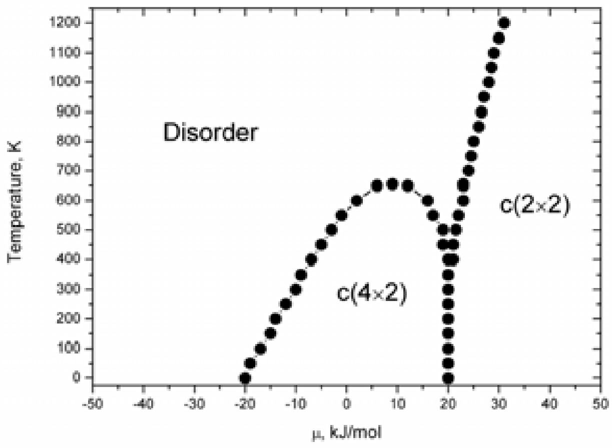


Fig. 2. Phase diagram of dimers adsorbed on square lattice.

References

[1]. Steele, W. A. The Interaction of Gases with Solid Surfaces // Pergamon Press: Oxford, 1974.

[2]. Su G. J., Zhang H. M., Wan L. J., Bai C. L., Wandlowski T. J.Phys.Chem. B. **2004**. v.108. p.1931.

[3]. Fefelov V.F., Gorbunov V.A. Myshlyavtsev A.V., Myshlyavtseva M.D. Chem. Eng. J. (**2009**) v.154 p.107.

[4]. Fefelov V.F., Gorbunov V.A. Myshlyavtsev A.V., Myshlyavtseva M.D. App. Surf. Sci. (**2009**) doi:10.1016/j.apsusc.2009.12.065

[5]. Roma F., Ramirez-Pastor A.J., Riccardo J.L. Langmuir (**2003**) v.19 p.6770.

CATALYTIC TRANSFORMATION OF METHANE (*VIA* CHLOROMETHANE) ON CATALYSTS BASED ON SAPOS AND HZSM-5 ZEOLITES

Gamero M., Mier D., Epelde E., Aguayo A.T., Bilbao J.

Chemical Engineering Department. University of the Basque Country. P.O. Box 644, 48080 Bilbao, Spain. Tel: 34-94-6015501. Fax: 34-94-6013500.
e-mail: mgyenes@hotmail.com

The activation of methane and subsequent conversion to higher hydrocarbons has received considerable research attention. Thus, the development of processes for chlorination of methane and posterior catalytic transformation of chloromethane, may reduce the economical drawbacks and high energy consumption associated with the valorization of natural gas via syngas [1]. Olefins yield, selectivity and deactivation on the catalytic transformation of chloromethane (MeCl) over SAPO-34, SAPO-18 and HZSM-5 zeolite (SiO_2/Al_2O_3= 30 and 80) have been studied [2,3].
The catalyst consists of 25 wt% of active phase agglomerated by wet extrusion with bentonite as binder (30 wt%) and inert alumina as charge (45 wt%).

The physical properties (Table 1) have been characterized by N_2 adsorption-desorption (Micromeritics ASAP 2000). The acid properties of the catalysts have been determined by measuring the differential adsorption of ammonia at 150 °C (DSC) and temperature-programmed desorption of ammonia (TPD) in a TG-DSC 111 (Setaram) connected on line to a mass spectrometer Balzers Quadstar 422 [4].

Table 1: Physical and acid properties of the catalysts.

Catalyst	Active phase	BET surface, m^2/g	V_P, cm^3/g	A_T, *	S_A, **
CS-18	SAPO-18	216	0.299	0.091	150
CS-34	SAPO-34	207	0.577	0.148	150
CHZ-30	HZSM-5 (SiO_2/Al_2O_3= 30)	208	0.649	0.252	120
CHZ-80	HZSM-5 (SiO_2/Al_2O_3= 80)	203	0.468	0.187	100

* A_T: Total acidity, mmol NH_3/g_{cat}; ** S_A: Average Strength Acidity, kJ (mol $NH_3)^{-1}$.

The reaction was carried out in a fixed bed reactor operated isothermally at atmospheric pressure in the 350-450 °C range and space time up to 15 (g of catalyst) h (mol $CH_2)^{-1}$. An adsorption packed with $CaCO_3$ was placed just after the reactor to trap the formed HCl. The products were analyzed by on line micro-chromatograph (Varian CP-4900). The coke deposited in the catalyst has been quantified by combustion in a SDT 2960 thermobalance of TA Instruments.

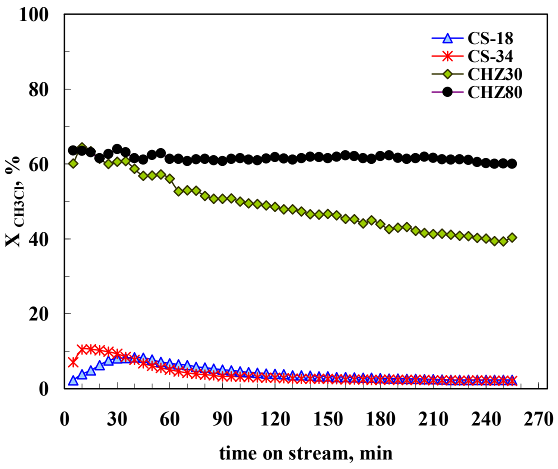


Figure 1: Evolution with time on stream of the conversion of MeCl using different catalysts. 350 °C; 5.8 (g of catalyst) h (mol CH_2)$^{-1}$; feed, pure MeCl; time on stream, 4 h.

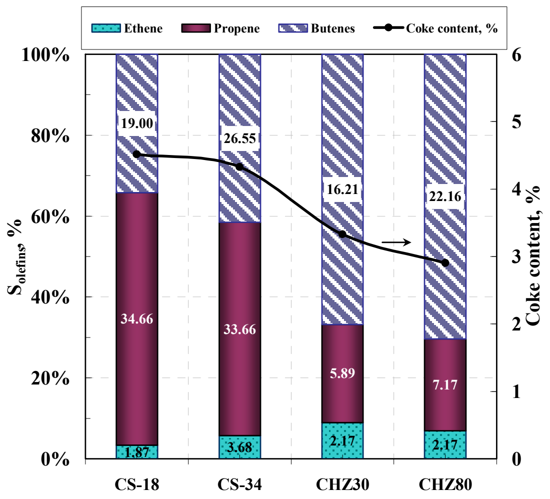


Figure 2: Individual olefin selectivity at zero time on stream and coke content deposited on the catalysts. 350 °C; space time, 5.8 (g of catalyst) h (mol CH_2)$^{-1}$; feed, pure MeCl; time on stream, 4h.

Catalyst of HZSM-5 zeolite (SiO_2/Al_2O_3 =80) presents a very slow deactivation in 4h in the MeCl (63 % of conversion calculated on a CH_2 basis) (Figure 1). This is a consequence of the moderate acid strength (Table 1) and low coke deposition in the pores of the catalyst (Figure 2). On the other hand, catalyst of HZSM-5 (SiO_2/Al_2O_3 =30) zeolite has a higher deactivation. This might be as a consequence of the higher acidity strength of the acid sites (Table 1). The severe shape selectivity of the SAPO-18 and SAPO-34 is decisive for the rapid deactivation (blockage of pores) by coke deposition of the corresponding catalyst.

Regarding olefin selectivity, the propylene is the major product for SAPO-18 (35 %) and SAPO-34 (34 %), whereas butenes are the major olefin for catalysts based on HZSM-5 zeolites (Figure 2).

Consequently, the catalytic transformation of methane (*via* chloromethane) is an interesting complementary route for the MTO process, in order to obtain light olefins on catalyst of HZSM-5 zeolite with a moderate acid strength.

References

[1]. Naccache C.M., Mériaudeau P., Sapaly G., Van Tiep L., Ben Taârit Y. *J. Catal.* **2002** *205* 217-220.

[2]. Noronha L. A., Falabella Souza-Aguiar E., Mota C.J.A. *Catal. Today* **2005** *101* 9-13.

[3]. Svelle S., Aravinthan S., Bjørgen M., Lillerud K., Kolboe S., Dahl M. I., Olsbye U. *J. Catal.* **2006** *241* 243-254.

[4]. Aguayo A. T., Gayubo A. G., Vivanco R., Olazar M. and Bilbao J. *Appl. Catal. A. General* **2005** *283* 197-207.

PP-III-22

TAILORING POLYMER PRODUCTS VIA LIVING POLYMERIZATION

Gomes V.G.

School of Chemical and Biomolecular Engineering, University of Sydney,
NSW 2006, Australia, vincent.gomes@sydney.edu.au

INTRODUCTION

Accurate control of product properties can be of great benefit to industry in producing targeted polymeric materials. Living polymerization via free radical mechanism (LFRP) provides opportunities to control polymer architecture and molar mass distribution, which are fundamental attributes of polymer materials. Block copolymers synthesized by LFRP offer the potential of tuning product properties precisely. Thus, chemically controlled living free radical polymerisation was tested with reversible addition–fragmentation chain transfer (RAFT), a most promising technique for industry[1-3]. RAFT is facilitated by compounds having structures such as Z-C(=S)S-R. During its pre-equilibrium stage, the addition of the initiator-derived propagating radical Pn^* to thiocarbonylthio reagent followed by forward fragmentation of the carbon centred intermediate radical gives rise to a polymeric RAFT moiety and a new radical $\mathbf{R}^*$. The process is followed by forward fragmentation of the intermediate radical giving rise to a polymeric RAFT agent and a new reinitiating radical, which reacts to produce a new propagating radical and extends the polymeric chain.

MODELLING

Our RAFT emulsion polymerization model accounts for reactions in the aqueous and particle phases during propagation, termination, transfer to monomer and RAFT exchange, along with radical absorption and desorption to and from particles. A ‘zero-one’ model was developed based on the consideration that the rate of radical-radical termination within a particle is fast relative to the rate of radical entry into particles. Thus a particle has either zero or one radical. Our model equations for the multi-phase system include governing equations for the aqueous phase, the organic liquid phase, the particle phase with the species balances and the energy balance over the reactor and the heating/cooling system. The mixed differential and integro-partial differential equations were solved using our developed software. The model predictions for a range of operational conditions were compared with our experimental results.

EXPERIMENTAL

We synthesized the RAFT agent (O-ethylxanthyl ethyl propionate) in our laboratory. Styrene, methyl and butyl acrylate monomers, initiator (sodium persulfate), purification column, and surfactant (sodium dodecyl sulfate) were obtained from Sigma-Aldrich (USA). In the first stage, polystyrene and polybutyl acrylate homopolymers were prepared with predetermined molecular weights. Emulsion polymerization was performed in a semi-batch reactor (at 60-80°C) with 350 rpm agitation speed, water, a buffer solution and monomer. Experiments were designed to produce polymeric latex particles containing macro-RAFT agent with a targeted molecular weight. In the second stage remaining reagents were added to the seed latexes from first stage to produce b-PBA-co-PSt. Monomer conversion was determined gravimetrically, the PSD was measured using PL-PSDA (PL-DG2) was molar mass with PL-GPC120. ^{1}H-NMR spectra (Brüker AM400) was used to analyse the polymer structure and composition.

RESULTS AND DISCUSSIONS

Experimental data were compared with model predictions to confirm our postulated mechanism and the properties expected from the reactor. Low molecular weight polymers of butyl acrylate prepared in the first stage was used as the polymeric RAFT agent to polymerize styrene in the second stage under batch and semi-batch emulsion conditions to provide well-defined block copolymers (b-PBA-co-PSt) with narrow molecular weight distributions. The process was optimized by performing semi-batch polymerization, in which the second monomer was gradually added to the reactor. This resulted in a block copolymer of high purity and relatively low polydispersity as compared with that produced under batch conditions. The choice of block sequence is important in reducing the influence of terminated chains on the distributions of polymers that were obtained. We found that polymerizing styrene first followed by the high active butyl acrylate monomer resulted in much purer block copolymer with low polydispersity as indicated by GPC and ^{1}H-NMR measurements.

References

[1]. Altarawneh, I.S., V.G. Gomes and M.S. Srour, (2008). Macromol Reaction Eng, 2(1): 58-79.
[2]. Charmot, D. et al., (2000). Macromolecular Symposia, 150(Polymers in Dispersed Media): 23-32.
[3]. Chiefari, J. et al., (1998). Macromolecules, 31(16): 5559-5562.

EFFECT OF CATALYSTS ON HIGH-ENERGY MATERIALS WITH A CHLORINELESS OXIDIZER BURNING

Arkhipov V.A.[1], Bespalov I.S.[2], Gorbenko T.I.[2], Kuznetsov V.T.[1], Savel'eva I.A.[1]

[1]Research Institute of Applied Mathematics and Mechanics
of Tomsk State University, 634050, Tomsk, Russia
[2]Tomsk State University, 634050, Tomsk, Russia
leva@niipmm.tsu.ru

Now due to the intensification of space-rocket activity the ecological requirements to high-energy materials (HEM) combustion products have sharply increased. One of perspective way to create the non-polluting HEM compositions is replacement of traditional used ammonium perchlorate by chlorineless oxidizer - ammonium nitrate (AN). To compensate the decrease of HEM power performances the nitramins, energetic binder (EB) and ultrafine aluminum powders are added into propellants.

The experimental research results of effect of condensed system compositions with chlorineless oxidizer and energetic binder on burning rate at atmospheric pressure are presented in this report. The analysis of catalysts effect on burning process, percentage and dispersity of aluminum powders on burning rate is carried out.

Experimental researches was carried out on two basic compositions with coefficient of oxidizer excess α =0.545. Basic compositions (are given in the table) contained ammonium nitrate, energetic additive (EA), energetic binder with its own coefficient of oxidizer excess α =0.407. The mechanical mixture of micron size aluminum powder (ASD-6 grade, specific surface A_{sp}=0.56 m^2/g) and an ultrafine aluminum powder ("Alex" grade, A_{sp} =15.5 m^2/g) was used as a metal fuel. In this research the catalysts: a silicon dioxide (SiO_2), soot and a mix of these catalysts in the ratio 1/1, was used. These catalysts were added in amount of 2 mass % over 100 % fuel mass.

HEM compositions were moulded with the help of fluoroplastic die by extrusion method. Cylindrical test-pieces with a diameter of 10 mm and height of (30-35) mm which density value spread did not exceed 0.02 g / sm^3 were used. Lateral surface of samples was covered with a solution of linoleum in acetone. The stationary burning rate was measured at atmospheric pressure.

Table

Base composition components	content, mass %	
	composition №1	composition №2
AN	27.5	30.0
EA	26.0	26.0
EB	30.5	24.0
Al	16.0	20.0

Experimental data shows, that adding of 2 mass % of a silicon dioxide in composition № 1, with total of aluminum amount of 16 mass %, promotes burning rate increase of (1.3-1.6) times. The adding of a silicon dioxide in propellant system results in increase of burning rate of samples the more strongly, the higher “Alex” fraction contents in metal fuel. Especially clearly this dependence is displayed in composition № 1. The soot adding influence is the most clearly displayed in fuel systems containing ASD-6. It is necessary to note, that the quantity of aluminum does not practically effect on efficiency of soot additive during burning process.

The analysis of experimental results shows that the most efficient burning rate control of the metallized propellants containing aluminum ASD-6 and "Alex" grades, based on chlorineless oxidizer, the energetic additive and energetic binder is possible by means of adding of silicon dioxide in amount of 2 mass % over 100 %. In compositions with an energetic binder is expediently to use the mixed metal fuel, especially by inletting additives that effect on the mechanism of initial aluminum combustion. It is shown, to ensure a high level burning rate of propellants, based on the mixed metal fuel, comparable with a burning rate level of propellant containing "Alex" as a metal fuel, the optimal ratio of ASD-6/"Alex" for composition № 1 is 40/60, and for composition № 2 is 50/50.

This work was carried out within the framework of realization of the Federal target program “The Scientific and scientific-pedagogical staff of innovative Russia” for 2009-2013 with a support of State contract П474 from 04.08.2009 “Developing and processing of the high-energy filled polymer compositions”.

PP-III-24

THE PROCESS FOR PRODUCING LACTIC ACID BY MEMBRANE BIOREACTOR SYSTEM

Ilushka I.V., **Kolbakov V.V.**

Nordbiochem Ltd, Polva, Estonia, agro3000@inbox.ru

Lactic acid has been manufactured by employing the batch-type fermentation process which comprises the steps of culturing lactic acid bacteria for more than 60 hours after inoculation and isolating lactic acid from the culture medium. The batch process has an advantage of high-concentration lactic acid production of over 120 g/L, though it has revealed a critical shortcoming of low volumetric productivity of less than 5 g/L/h. To compensate for the low productivity, the fermentation volume is enlarged, which in turn increases the cost for the construction of fermentation facilities and the maintenance of the facilities. As an alternative approach to overcome the low productivity of batch-type fermentation process, cell-recycling process by which microorganisms are concentrated in a fermenter to increase the productivity, has been suggested.

According to present experiments, the lactic acid can be produced in a simple and inexpensive manner, so as to eliminate the disadvantages of the prior processes discussed above. It has been surprisingly found, that if to create such conditions at which growth rate of cells is minimal but sufficient for replacement cells death, in this case decrease of the specific consumption of carbohydrates per unit of lactate is take place.

The growth rate of cells can be reduced by increase of temperature and decrease of pH up to critical and supercritical values for each microorganism and as well by decrease of amounts nutrients fed into the fermenter and by use of additives bacteriostatics.

It has been surprisingly found, that for each microorganism there are optimal conditions - temperature, pH, amounts of nutrients and bacteriostatics fed into the fermenter, at which growth rate of cells is minimal but sufficient for replacement cells death.

Preferably, the optimal growth rate of cells reach by combination of temperature, pH, by amount of used nutrients and bacteriostatics fed into the fermenter.

Concentration of cells of microorganisms has been reached value 100 g/L (dried cell weight) and more, in the membrane recycle bioreactor system. With combinations of parametres described above, we can get volumetric productivity more 100 g/L/h.

CO REMOVAL AT THE MICROSCALE: A 1-CENT GOLD PROX REACTOR

Jiménez N.[1], **López E.**[1], **Trifonov T.**[2], **Rodríguez A.**[2], **González de Rivera F.**[3], **Rodríguez L.I.**[3], **Seco M.**[3], **Rossell O.**[3], **Llorca J.**[1]

[1]Institut de Tècniques Energètiques, Universitat Politècnica de Catalunya
Av. Diagonal 647, Ed. ETSEIB, 08028 Barcelona, SPAIN
Fax: (0034)934017149, E-mail: jordi.llorca@upc.edu
[2]Departament d'Enginyeria Electrònica, Universitat Politècnica de Catalunya
[3]Departament de Química Inorgànica, Universitat de Barcelona

Introduction

The growing implementation of fuel cells for new portable electronic devices has moved research into improving reformers for in-situ hydrogen production, separation and purification. It is well-known that Pt-based anodes of fuel cells are easily poisoned by CO. In this context, CO preferential oxidation (COPROX) is the preferred final step to purify hydrogen streams from small-scale reformers [1].

In recently pioneering publications we reported an innovative miniaturization for hydrogen production based on silicon micromonoliths [2,3]. This novel substrate contains millions of regular and parallel circular microchannels per square centimeter which results in a specific contact area ca. 100-fold larger than that of conventional microreactors. These features solve the problem of moving down the scale and, at the same time, increasing the reaction area available. Moreover, high heat transfer rates are achieved due to the good thermal conductivity of silicon. In this work we report a silicon micromonolith loaded with Au/TiO_2 catalyst for low-temperature COPROX aimed at downstream hydrogen purification for PEMFC feeding.

Functionalization of silicon micromonoliths

Silicon micromonoliths (13 mm in diameter, 0.2 mm height, see figure 1) were prepared by photoassisted electrochemical etching which led to a substrate with $>10^6$ straight and parallel circular channels of 3.3 micrometers in diameter. The micromonoliths were thermally oxidized to form a thin SiO_2 layer on the channel walls. A titanium dioxide layer was then deposited by decomposition of an alkoxide precursor. Given the well-known ability of gold nanoparticles deposited on oxide supports, such as TiO_2, to selectively oxidize CO in H_2-rich environments [4], Au nanoparticles capped with dendrimer were anchored on TiO_2. The catalyst and the functionalized silicon micromonoliths were characterized by scanning electron microscopy, focused ion beam, transmission electron microscopy, X-ray photoelectron spectroscopy and X-ray diffraction.

Catalytic tests

Before catalytic testing, the catalytic layer was activated by thermal treatment at 473 K for 2 h with a temperature gradient of 2 K min^{-1} under a carbon monoxide-air mixture diluted in argon (CO:Air molar ratio 1.3:6, contact time 0.15 s). For catalytic testing, silicon micromonoliths were glued with epoxy into stainless steel washers (external diameter 19 mm, internal diameter 7 mm), which were then incorporated within a stainless steel housing inside a furnace. Catalytic tests were carried out under different concentrations of H_2, CO and air in the inlet mixture. The H_2:CO molar ratio was varied from 1:1 to 20:1 to infer the influence of H_2 on the COPROX reaction simulating fuel cell operation. An equimolar ratio O_2:CO in feed was mantained in all experiences. Reaction tests were performed at 363 and 398 K.

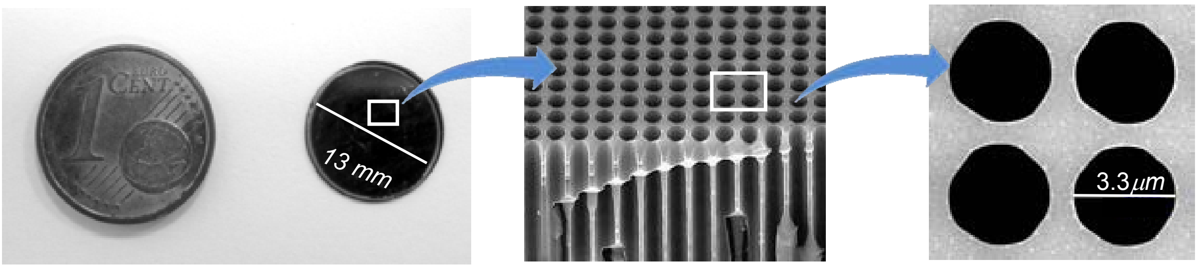


Fig. 1. Functionalized silicon micromonolith (left). Regular array of circular channels with depth/diameter ratio >65 (center). Detail of the reproducible channels of 3.3 μm in diameter (right).

For an inlet mixture H_2:CO~20:1, CO conversions were ca. 20 and 33% at 363 and 398 K, respectively. The latter represents ~1 NmL$_{CO}$ converted per minute and per mL of microreactor. After ca. 65 h under reaction no deactivation was observed.

References

[1] O. Korotkikh, R. Farrauto; *Catal. Today:* **2000**, 62, 249.
[2] J. Llorca, A. Casanovas, T.Trifonov, A. Rodríguez, R. Alcubilla; *J. Catal:* **2008**, 228-233.
[3] E. López, A. Irigoyen, T. Trifonov, A. Rodríguez, J.Llorca; Int. J. Hyd. Energy, **2010**, in press.
[4] M. Haruta, M. Daté; *Appl. Catal. A,* **2001***,* 222, 427-437.

Acknowledgements

Financial support from MICINN (CTQ2009-12520 and TEC2008-02520) is acknowledged. N.J. is grateful to UPC for a PhD grant.

HYDROGEN PRODUCTION FROM METHANOL USING STRUCTURED CATALYSTS

Kawamura Y.[1,2], Ogura N.[1,2], Igarashi A.[1]

[1]*Department of Applied Chemistry, Kogakuin University, Tokyo 192-0015, Japan,*
E-mail: igarashi@cc.kogakuin.ac.jp
[2]*CASIO Computer Co., Ltd., Tokyo 198-0022, Japan*

Introduction. Microreactor systems based on a microchannel as a structured catalytic reactor have generated particular interest [1]. The microreactor allows reactions that are difficult to realize using conventional fixed-bed reactors, and is also suitable for integration with the various additional components required for operation using microfabrication technologies. Small polymer electrolyte fuel cells (PEFCs), a promising clean and high-efficiency power source for portable electrical devices, require a reformer to produce hydrogen by the steam reforming of alcohols, hydrocarbons, or other fossil fuels. Such reformers typically have complex structures and have proven difficult to miniaturize. In the present study, a microreactor is proposed for use as a novel hydrogen producer for small PEFC systems.

Hydrogen production using a microreactor. The reduction of heat loss in the microreactor is the primary requirement for improving system efficiency, since heat release in microreactors is higher than in conventional reactors due to the increased specific surface area. The high-performance $Cu/ZnO/Al_2O_3$ catalyst prepared for the present methanol reformer under optimized conditions of the temperature and pH of precipitation and the addition of boehmite achieves hydrogen production at 20–25 °C lower temperature than a commercial copper catalyst. The catalytic activity was found to depend on the copper surface area, which is related to the amount of Cu dispersed within ZnO. Dispersion of Cu is promoted by precipitation at low temperature, which results in the formation of small crystallites of the precursor. Enlarged BET surface area by the addition of boehmite derives high catalytic activity. Under optimized pH, it is predicted that the excess of Cu species existing as amorphous-like malachite in the precursor, in addition to aurichalcite, facilitates the dispersion of Cu [2]. The miniaturized methanol reformer developed to utilize this $Cu/ZnO/Al_2O_3$ catalyst consists of a catalyst-coated microchannel in a serpentine arrangement, with total length of 333 mm and cross-section of 0.6×0.4 mm^2. The length of the microchannel was determined based on one-dimensional mass and heat balance analyses. The microreactor was fabricated from silicon and glass substrates using a number of microfabrication techniques. Sandblasting was found to be the most suitable of the preparation methods tested for microchannel formation, allowing microchannels to be processed quickly and leaving a desirable surface with microscale roughness for subsequent catalyst deposition. Catalyst adhesion is also promoted by the natural formation of a boehmite layer at the catalyst/substrate interface. Selective deposition of the catalyst in the microchannel is achieved by employing a photolithography technique, and complete contact between the silicon and glass substrates forming the reactor is ensured by employed an anodic bonding process. The overall size of the microreactor is $25\times7\times1.3$ mm^3, suitable for application as a power source in portable electronic devices. Methanol reforming using this reactor has also been demonstrated to reach the levels necessary to power a 1 W-class small PEFC system [3]. A multilayered microreactor integrating the miniature methanol reformer with a CO remover (consisting of a commercial noble metal catalyst), a catalytic combustor as a heat source for methanol reforming, vaporizers, and several necessary functional elements for hydrogen production has also been successfully fabricated at a size that achieves high thermal efficiency. The prototype miniature reactor system has dimensions of 22 mm (L) × 21 mm (W) × 10.7 mm (H), and has been demonstrated to produce hydrogen at a rate sufficient to generate electrical power of 2.5 W based on self-heating by the internal catalytic combustor [4]. Rapid start-up of methanol reforming using the $Cu/ZnO/Al_2O_3$ catalyst has also been shown to be feasible under an oxidative atmosphere, for which the durability of the catalyst can be improved by the addition of iron to the catalyst composition [5].

Conclusions. The microreactor, comprised of a catalyst-containing microchannel prepared using microfabrication technologies, achieved hydrogen production at rates suitable for driving a small polymer electrolyte fuel cell several watts.

References

[1]. W. Ehrfeld, V. Hessel, H. Löwe, *Microreactors*, Wiley-VCH, Weinheim, Germany, (**2000**).

[2]. Y. Kawamura, N. Ogura, K. Yamamoto, T. Katsumata, A. Igarashi, *J. Power Sources*, **2005**, 150, 20-26.

[3]. Y. Kawamura, N. Ogura, T. Yamamoto, A. Igarashi, *Chem. Eng. Sci.*, **2006**, 61, 1092-1101.

[4]. Y. Kawamura, N. Ogura, T. Terazaki, K. Yamamoto, T. Yahata, T. Yamamoto, A. Igarashi, *J. Chem. Eng. Japan*, **2005,** 38, 854-858.

[5]. Y. Kawamura, T. Ishida, W. Tezuka, A. Igarashi, *Chem. Eng. Sci.*, **2008**, 63, 5042-5047.

Acknowledgements

The work was carried out with the cooperation of Casio Computer Co.

NON CATALITIC PRODUCTION OF BIODIESEL

Khanikyan V.[1], **Kurkina A.**[2], **Kustov A.**[3], **Shvets V.**[4], **Sapunov V.**[5]

D.I. Mendeleev University of Chemical Technology of Russia,
Chair of Petrochemical Synthesis, 9 Miusskaya Square, Moscow, 125047, Russia,
tel/fax +7(499)978-95-54
[1]vagokhan@rambler.ru, [2]ak040387@mail.ru, [3]koustov@muctr.edu.ru
[4]hxc@muctr.ru, [5]sapunovvals@gmail.com

The growing production of the Biodiesel (BD) and growing contents of fatty acid methyl esters (FAME) in Biodiesel compositions needs ecologically beneficial Biodiesel technologies, based on the principles of "Green Chemistry" (the creation of waste less technologies). As is known, the traditional technology of BD have several disadvantages, one of which is a lot of wastes and difficulties on the stages of separation of the products of transesterification reaction like: glycerol, mono-, di-glycerides, biodiesel, and salts of fatty acids. The problem of separation is complicating if for rational use and for improving of economic indicator the manufacturers use waste vegetable oil as a raw material (after restaurant and Fast-foods) with a high content of free fatty acids.

As an alternative solution of this problem, we decided to divide the process of production of Biodiesel from vegetable oil into two stages. On the first stage the vegetable oil was hydrolyzed, and after a mixture of free fatty acids, mono, di- and three glyceride formation the product was mixed with methanol. By varying the pressure, temperature and time of the reaction the yield of methyl esters of fatty acids after the second stage was determined.

In two stages process there is no problem in separation and isolation of the reaction products. The other preference of two stages process is high rates of the both stages of hydrolysis and the final FAME formation without any special catalyst. The character of the reaction of esterification with methanol clearly shows autocatalytic contribution of the free fatty acids.

Thus, comparing the rate of esterification with the sum of rates of hydrolysis and subsequent esterification, we concluded that the design of two stages technology will be very interesting, profitable and environmentally feasible.

PP-III-28

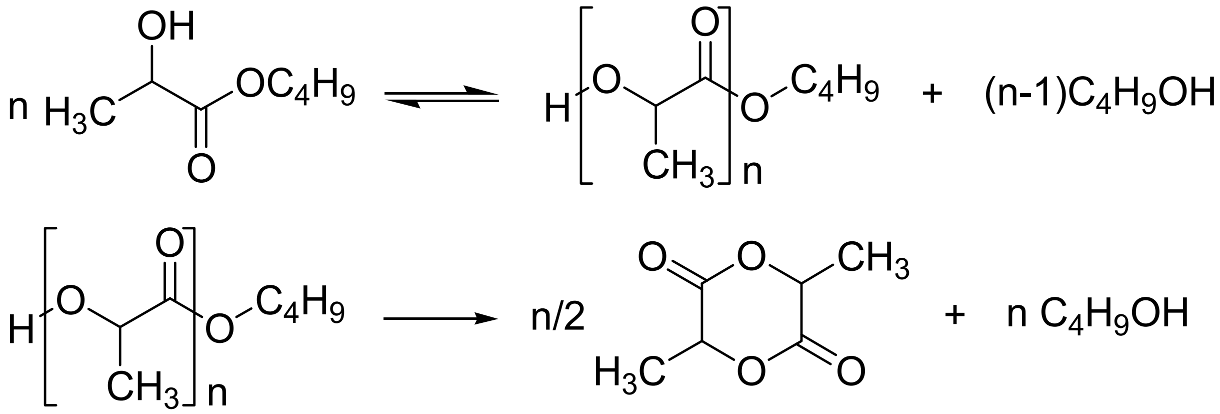
REACTORS FOR SYNTHESIS OF LACTIDE FROM BUTIL LACTATE

Khlopov D.[1], Shvets V.[2], Kozlovskiy R.[3], Suchkov Y.[4]

D.I. Mendeleev University of Chemical Technology of Russia,
9 Miusskaya Square, Moscow, 125047, Russia,
[1]hlopovd@mail.ru, [2]hxc@muctr.ru, [3]rakozlovskiy@mail.ru, [4] hxc@muctr.ru

Introduction

The best solution of the problem of polymeric wastes is replacement of petrochemical polymers with bio-degradable polymers. One of the most promising such polymers is polylactic acid (PLA) which can be synthesized from L-butil ester of lactic acid which in turn is produced by fermentation of renewable source. At present the most economical way to produce PLA is known to be polymerization of L-Lactide. The process of L-lactid production consists in catalytic synthesis of oligomers of butil ester of lactic acid (BLAO) by polycondensation of butyl lactate followed by catalytic depolymerization of BLAO. This two-step process is described by following chemical reactions:



Suitable catalysts for both stages are some compounds of metals of Groups IV, V or VIII of the Periodic Table. The concentration of the catalysts is about 0,5-3,0 % wt (counting on metal).

Experiment

For both of reactions the three types of reactor were investigated:

1) Semibatch mixed reactor;
2) Rotor film evaporator;
3) Molecular distillation evaporator.

Different reaction conditions had been varied for these reactors in both stages of process: temperature, pressure, type of catalyst, contact time, medium.

Results

The best results on synthesis of BLAO were obtained in the semibatch mixed reactor. The process can be carried out catalytically under temperature 170-180°C. Reaction should be conducted preferably under continuous flow of N_2 in order to facilitate butanol removing. This method provides to produce BLAO with degree of oligomerisation in the range of n = 9-10; with yield up to 95% and specific capacity about 15-20 g (BLAO)/(l×h). The most active catalyst on this stage is tin (II) octoate with concentration 0,5% wt.

The best results on synthesis of lactide were obtained in the molecular distillation evaporator working in the continuous flow regime. The process preferably was carried out with catalyst witch was added on the stage of producing BLAO under vacuum (pressure = 1-5 torr) and temperature 220°C. This method provides to produce lactide with yield up to 90 % and specific capacity of reactor (concerning evaporation surface) 3,5 kg(lactide)/(m2×h).

Conclusions

The three types of reaction units were examined for two reactions: oligomerisation of butyllactate and formation of lactide. The best reactor type and reaction conditions were experimentally determined for both of processes.

AQUEOUS PHASE REFORMING OF BIOMASS DERIVED ALCOHOLS AND POLYOLS TO HYDROGEN AND FUEL COMPONENTS

Kirilin A.[1], **Tokarev A.**[1], **Salmi T.**[1], **Mikkola J.**[1,2], **Murzin D.**[1]

[1]*Laboratory of Industrial Chemistry and Reaction Engineering, Åbo Akademi University,Turku, Finland, akirilin@abo.fi*
[2]*Department of Chemistry, Technical Chemistry, Chemical Biological Centre, Umeå University, Umeå, Sweden*

Processing of biomass-derived compounds for the production of various valuable chemicals is nowadays of high importance [1]. Aqueous phase reforming (APR) of oxygenated hydrocarbons originating from biomass is among promising methods to produce hydrogen [2] and components of liquid fuels [3]. However, conversion of renewables via APR often faces a number of challenges including the development of effective, selective and stable catalyts, process technology etc. Understanding of the process chemistry, e.g. the influence of the feed nature, the identification of products and intermediates, their transformations, is an essential step towards improved process effeciency.

In the present work aqueous phase reforming of various oxygenates derived from biomass: bioethanol, glycerol and sorbitol (10 wt.% solutions in water was studied). Continuous stainless steel reactor (fixed bed) was applied to investigate the performance of 5 wt.% Pt/Al_2O_3 catalyst (dispersion 34%) at a space velocitiy of 0.6 -3 h^{-1} at 225°C and 2.93MPa (carrier gas N_2).

For APR of ethanol, a conversion of 99% of the starting material was reached, however, methane formation was found to be very prominent. Its formation can proceed through initial ethanol dehydrogenation to acetaldehyde, which in turn undergoes decarbonylation to form methane and CO (yield 0.1 mmol/min). Under the experimental conditions, carbon monoxide reacts with water via water-gas shift reaction producing CO_2 and H_2, which were observed in reasonable amounts (0.44 and 0.22 mmol/min, respectively). Changing the feedstock to glycerol, the level of conversion and H_2 formation remained constant whereas much less methane formation was observed (0.078 mmol/min) implying that glycerol is a more feasible renewable feed for the APR process.

The main focus was put on the conversion of sorbitol as the most promising raw material for the APR process due to the possibility of obtaining transportation fuel components (hexane etc) and better ratio between H_2 and CO_2 in reforming process followed by WGS reaction. The content of carbon in the liquid phase detected by total organic carbon analysis (Fig. 1) decreases with an increase of the space velocity from 73 to 2%. The hydrogen yield (19 to10%) and formation of CO_2 (selectivity 62–88%) are linearly dependent on the space velocity and decreased with an increase of contact time. Similar tendencies were observed for the hydrocarbons formation, but their total yield did not exceed 4%. The level of carbon monoxide detected during APR of sorbitol was very low, thus sorbitol is a suitable raw material for production of CO-free hydrogen. The presence of molecules with different functional groups such as aliphatic alcohols, ketones, furane and pyrane derivatives as well as saturated cyclic esters was observed in the liquid phase, which implies that APR may be considered as a feasible method for the production of liquid fuel components. By altering the process parameters under various experimental conditions, it is possible to tune the APR process for a selective production of various desired products.

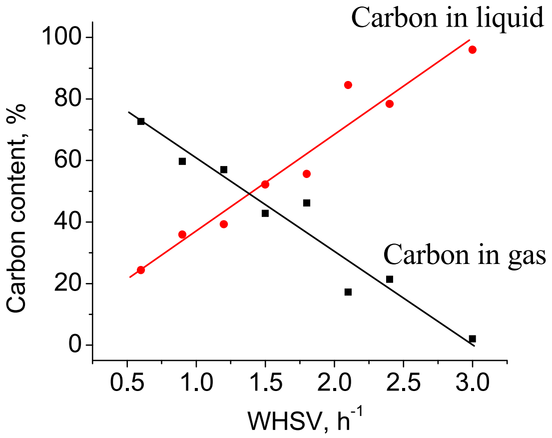


Figure. 1. Carbon content in the gas and liquid phase as a function of the space velocity

It can be concluded, that APR is an attractive method for hydrogen/hydrocarbons production from renewables such as bioethanol and various polyols. However, high methane formation in the case of ethanol and low hydrogen yields makes this raw material less efficient. Sorbitol and glycerol are feasible and abundant raw materials for hydrogen production at a very low level of CO and components of transportation and stationary fuels. Moreover, the possibility to influence the gas and liquid phase composition by altering the process conditioins can essentially improve energy production from biomass-derived materials.

References

[1] D.A. Simonetti, J.A. Dumesic, *Catal. Rev.*, **2009**, 51, 441-484.
[2] R.M. West, E.L. Kunkes, D.A. Simonetti, J.A. Dumesic, *Catal. Tod.*, **2009**, 147, 115-125.
[3] R.D. Cortright, R.R. Davda, J.A. Dumesic, *Nature*, **2002**, 418, 964-967.

Acknowledgements

The National Research Agency for Innovation and Technology (TEKES), Fortum Foundation, the Academy of Finland in collaboration with the Northern European Innovative Energy Research Programme (N-Inner) are gratefully acknowledged for financial support.

PP-III-30

METHOD FOR COMPLEX PROCESSING OF POLYMERIC WASTES INTO FUEL FRACTIONS

Korneev I.S.[1], **Kozlovsky R.A.**[2], **Suchkov J.P.**[3], **Shvets V.F.**[4], **Romanova A.V.**[5], **Khlopov D.S.**[6], **Danilov I.V.**[7], **Sidorov A.M.**[8], **Yuzhnov N.M.**[9]

D. Mendeleyev University of Chemical Technology of Russia, Moscow, Russia
[1]*iskorneev8282@mail.ru*, [2,3,4,5,6]*hxc@muctr.ru*, [7,8,9]*danilov@nikiet.ru*

Introduction

At present time one of the main ecological problems is permanently growing volume of polymeric wastes, particularly tire-cover rubber and isoprene rubber. There are several methods for utilization or treatment of those: recycling, burial, combustion, processing into useful products. Evidently the burial and combustion are eco-faulty technologies and recycling and processing are more ecological friendly ones. The problem is that only a limited part of rubber can be recycled. Hence it would be preferred the rest amount of wastes to be converted into useful products. Today the main trend in development of such technologies is toward processing of rubber wastes into hydrocarbon material which can be used as source for fuel fractions.

In this report two lab-scale installations for thermal processing of some rubber are presented.

Experimental section

Two installations were built up: (1) Reaction-distilling unit consists of batch-type reactor supplied with stirrer and reflux column. Thermal destruction proceeds at temperature 400-450 °C. The reflux column provides to output target fraction of products having boiling point lower then 330 °C. (2) Reaction-distilling unit consists of continuous reactor supplied with stirrer and reflux column. This reactor is combined with a screw feeder mixture of rubber and solvent-coreactant. Preliminary homogenizing the mixture of rubber and solvent-coreactant occurs in the screw feeder. After this operation reaction mixture goes to Reaction-distilling unit.

As a feed stock the following materials were used: tire-cover rubber (total sulfur content is 1.3-2.4 %) and isoprene rubber (total sulfur content is 0.8-1.5 %).

As a catalyst we tested solid materials based on zinc oxide supported on solid carrier. As an adsorbent for sulfur-containing substances we tested solid systems containing Ca, Zn, Al and their oxides.

As a solvent-coreactants we had been used waste mineral oils and products of destruction of rubber.

Results

The presented technology provides almost 100 % conversion of organic part of feed stock. At that the yield of liquid products is 40-60 % for rubber material (the content of sulfur in products is 0.4-1.1 %). Liquid products have a composition and boiling point range close to those of fuel fractions.

Liquid products of destruction contain 25-35 weight % of hydrocarbons with a boiling point less 185 °C and 35-45 weight % of hydrocarbons with a boiling point 180-320 °C.

The liquid products of destruction of rubber boiling below 185 °C contain about 55-65 % of uncondensed aromatics and fraction boiling in the range 185-300 °C contain about 10-20 % of condensed aromatics.

In order to convert products of polymer's destruction into components of fuel fractions it was necessary remove unsaturated and sulfur compounds by means of hydrogenation hydrodesulfurization. The hydrotreating was carried out in the autoclave. The hydrogenation of unsaturated hydrocarbons was carried out under 300-340 °C and 25-40 bar in the presence of Al-Co-Mo heterogeneous catalyst that provided 80-95% conversion of double bonds. The hydrodesulfurization was resulted in 80-95 % degree of sulfur removing.

Conclusion

The results obtained allow formulation of general approach to technology of thermal and thermal-catalytic processing of polymeric wastes into fuel fractions.

FUEL PRODUCTION BY HYDROTREATING OF TRIGLYCERIDES ON NiMo/Al_2O_3 CATALYST

Sándor Kovács[1], **Artur Thernesz**[2], **Jenő Hancsók**[1]

[1]MOL Institutional Department of Hydrocarbon and Coal Processing,
Pannon University, P.O. Box 158., H-8201, Veszprém, Hungary,
e-mail: hancsokj@almos.uni-pannon.hu
[2]MOL Hungarian Oil and Gas Plc., DS Development, P.O. Box 1.,
2443 Százhalombatta, Hungary

The applicability of vegetable oils and their derivates as automotive fuels has been well-known for a long time. In the recent years, intensive studies have been started for the replacement of biodiesels (fatty acid methyl esters). Biodiesels are the almost exclusively used bio blending components in diesel fuels nowadays; however, they have numerous disadvantages during the production and application. One of the solutions can be the hydrogenation of different triglyceride containing feedstocks and their conversion into “bio gas oil” with heterogeneous catalyst. The bio gas oil is a mixture of hydrocarbons (especially normal and isoparaffins) having boiling points similar to diesel fraction, obtained from triglycerides (e.g. vegetable oils, used cooking oils, animal fat). The research, production and application of these second generation biofuels are intensively subsided by the European Union [1-6]. That’s why in the last couple of years intensive research and development efforts were started to find other thermal and/or catalytic routes of converting triglyceride-containing feedstocks into fuels which have a different chemical structure and better quality than the fatty acid methyl esters. However, many questions are still unclear [7-10].

According to these, our aim was to investigate the applicability of an expediently modified NiMo/Al_2O_3 catalyst promoted with fluoride and phosphorus for the conversion of specially pretreated Hungarian sunflower oil to produce motor fuels. The experiments were carried out in bench-scale apparatus in continuous operation.The changes of the hydrocracking (olefinic double bond saturating, oxygen removing, isomerization) activity of the applied catalyst, the pathways of hydrodeoxigenation reactions and the effect of process parameters (temperature, pressure, LHSV) on the yield and on the quality of the products were also investigated. The range of the applied process parameters – based on our preliminary experiments – were the following: temperature: 300-380°C, pressure: 60-90 bar, LHSV: 1.0-3.0 h^{-1}, H_2/sunflower oil volume ratio:400-600 Nm^3/m^3.

It was concluded that on the investigated catalyst products with high (>60%) paraffin content having boiling points similar to diesel fraction (T = 360-380°C, p = 60-90 bar, LHSV = 1.0-1.5 h^{-1}, H_2/sunflower oil volume ratio: 500 Nm^3/m^3) could be produced. In case of every investigated process parameter the C_{18}-, C_{16}-, C_{17}- and C_{15}- paraffins were formed, i.e. on the applied catalyst both the HDO and the decarboxylation/decarbonylation (DECARB) reactions took place.

References

[1]. Demirbas, A.: „Biorefineries: Current activities and future developments", Energy Conversion and Management, 2009, 50, 2782–2801

[2]. Hayes, D.J.: „An examination of biorefining processes, catalysts and challenges", Catalysis Today, 2009, 145, 138–151.

[3]. Hancsók, J., Krár, M., Magyar, Sz., Boda, L., Holló, A., Kalló, D.: „Investigation of the production of high cetane number biogasoil from pre-hydrogenated vegetable oils over Pt/HZSM-22/Al_2O_3", Microporous and Mesoporous Materials, 2007, 101(1-2), 148-152.

[4]. Balat, M., Balat, H.: „A critical review of bio-diesel as a vehicular fuel", Energy Conversion and Management, 2008, 49, 2727–2741.

[5]. S. Jain, M.P. Sharma: „Stability of biodiesel and its blends: A review", Renewable and Sustainable Energy Reviews, 2010, 14, 667-678.

[6]. Commission of the European Communities, COM(2006) 34 final, 2006.

[7]. Craig, K.W., Sorevan, W.D.: "Production of hydrocarbons with relatively high cetane rating", 1991, US 4,992,605.

[8]. Donnis, B., Egeberg, R.G., Blom,P., Knudsen, K.G., Hydroprocessing of Bio-oils and oxygenates to hydrocarbons. Understanding the reaction routes", Topics in Catalysis, 2009, 52, 229-240.

[9]. Gusmao, J., Brodzki, D., Djéga-Mariadassou, G., Frety, R.: „Utilization of vegetable oils as an alternative source for diesel-type fuel: hydrocracking on reduced Ni/SiO_2 and sulphided Ni-Mo/γ-Al_2O_3", Catalysis Today, 1989, 5, 533-544.

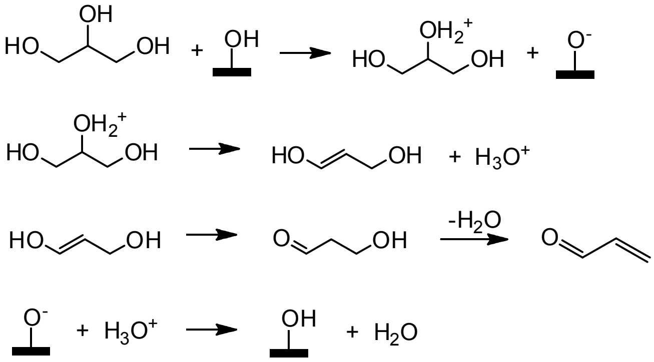
[10]. Liu, Y., Sotelo-Boyás, R., Murata, K., Minowa, T., Sakanishi, K.: „Hydrotreatment of Jatropha Oil to Produce Green Diesel over Trifunctional Ni–Mo/SiO_2-Al_2O_3 Catalyst", Chemistry Letters, 2009, 38 (6), 552-553.

CONVERSION OF GLYCEROL TO VALUE-ADDED CHEMICALS OVER POLYOXOMETALATE CATALYSTS

Kozhevnikov I.V., Alhanash A., Kozhevnikova E.F.

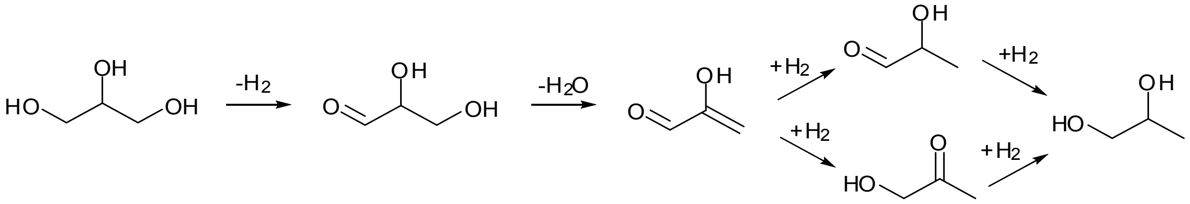
Department of Chemistry, University of Liverpool, Liverpool, L69 7ZD, UK
E-mail: kozhev@liverpool.ac.uk

The production of chemicals by catalytic transformation of bio-resources is a global challenge. Recent development of biodiesel production by transesterification of plant oils and animal fat has made a large amount of glycerol available as a renewable feedstock for the synthesis of value-added chemicals. One of the most important directions for the utilisation of glycerol is its dehydration to acrolein. We found that caesium 12-tungstophosphate, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (CsPW), possessing strong Brønsted acid sites is an active catalyst for the dehydration of glycerol to acrolein in the gas-phase at 275°C and 1 bar pressure [1]. The initial glycerol conversion amounts to 100% at 98% acrolein selectivity, however, decreases significantly with the time on stream (~40% after 6 h) due to catalyst coking, without impairing acrolein selectivity. Doping CsPW with platinum group metals (PGM) together with co-feeding hydrogen improve catalyst stability to deactivation, while maintaining high selectivity to acrolein. The enhancing effect of PGM was found to increase in the order: Ru ~ Pt < Pd. The catalyst 0.5%Pd/CsPW gives 96% acrolein selectivity at 79% glycerol conversion, with a specific rate of acrolein production of 23 mmol $h^{-1}g_{cat}^{-1}$ at 275°C and 5 h time on stream, exceeding that reported previously for supported heteropoly acids (5 – 11 mmol $h^{-1}g_{cat}^{-1}$ per total catalyst mass). Evidence is presented regarding the nature of acid sites required for the dehydration of glycerol to acrolein, supporting the importance of strong Brønsted sites for this reaction (Scheme 1).



Scheme 1. Mechanism of glycerol dehydration on Brønsted acid sites.

Hydrogenolysis of glycerol to 1,2-propanediol (1,2-PDO) and 1,3-propanediol (1,3-PDO), which are important commodity chemicals currently produced from petroleum derivatives, has attracted significant interest. We found that ruthenium-doped CsPW is an active bifunctional catalyst for the one-pot hydrogenolysis of glycerol to 1,2-PDO in liquid phase, providing 96% selectivity to 1,2-PDO at 21% glycerol conversion at 150°C and an unprecedented low hydrogen pressure of 5 bar. Rhodium catalyst, 5%Rh/CsPW, although less active, shows considerable selectivity to 1,3-PDO (7.1%), with 1,2-PDO being the main product (65%). The reaction probably occurs via dehydrogenation of glycerol to glyceraldehyde followed by dehydration to 2-hydroxyacrolein and its hydrogenation to yield 1,2-PDO (Scheme 2) [2].



Scheme 2. Proposed mechanism for glycerol hydrogenolysis over Ru/CsPW.

References

[1]. A. Alhanash, E.F. Kozhevnikova, I.V. Kozhevnikov, Appl. Catal. A **2010**.

[2]. A. Alhanash, E.F. Kozhevnikova, I.V. Kozhevnikov, Catal. Lett. **2008,** 120, 308.

Acknowledgements

Financial support from the EPSRC (research grant EP/E039847) is gratefully acknowledged.

PHOTOCATALYTIC HYDROGEN PRODUCTION FROM WATER SOLUTION OF GLYCEROL

Ekaterina Kozlova[1,2], Tatyana Korobkina[1], Alexander Vorontsov[1,2]

[1]*Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia, pr. Lavrentieva, 5,*
kozlova@catalysis.ru
[2]*Novosibirsk State University, Novosibirsk, Russia, Pirogova 2*

In recent years there have been intensive efforts toward the development of novel technologies for the production of hydrogen from renewable resources, mainly water and biomass. Among the various biomass-derived compounds proposed as feedstock for hydrogen production, glycerol ($C_3H_8O_3$) is of special interest because it is produced in large amounts (10 wt.%) as by-product of the chemical reaction (transesterification) in which vegetable oil is processed into biodiesel [1]. One of the most promising method of the simultaneous hydrogen production and glycerol utilization is the photocatalytic oxygen free glycerol destruction. It is carried out on the surface of a semiconductor photocatalyst with a noble metal (e.g. Pt/TiO_2) according to the equation:

$$C_3H_8O_3 + 3H_2O = 3CO_2 + 7H_2.$$

In this work, we aimed at the investigation of photocatalytic hydrogen production from water solution of glycerol under UV-light irradiation. Photocatalytic hydrogen emission from glycerol solution was carried out by the following method. Water suspension with 1%Pt/TiO_2 catalyst and glycerol was placed in a sealed thermostatic reactor without oxygen and illuminated by a 1000 W high-pressure mercury lamp under continuous stirring. Glycerol concentration varies from 6 to 60 mM, catalyst concentration was 0.75 g/L, temperature 20°C. Concentration of hydrogen was measured by means of gas chromatograph LChM-8. We obtained the dependence of the initial hydrogen evolution rate vs. initial glycerol concentration. One can see that the rate of the hydrogen production grows with the initial concentration at the low initial concentrations and practically does not change at the initial concentrations above 12 mM, that corresponds to Langmuir-Hinshelwood mechanism.

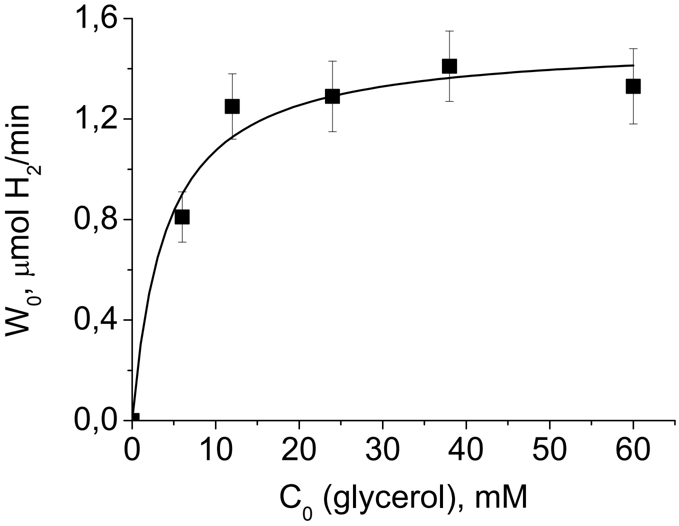


Fig. 1. Initial hydrogen emission rate vs. the initial glycerol concentration.

This figure represents that the rate of the photocatalytic hydrogen production quite high. However, the production of hydrogen using Pt/TiO_2 catalysts has a big disadvantage: titania based catalysts absorbs UV-light only. In order to shift the band gap of titania we doped titania by $Zn_xCd_{1-x}S$ solid solutions. The combination of these metal sulfides nanoparticles is easy to synthesize and exhibit absorption and emission properties in a wide wavelength region that allows one to vary the band gap value. Platinum was deposited on the surface of these materials as a co-catalyst for the hydrogen production. These catalysts were characterized by XRD, XPS and UV-vis spectroscopy techniques. The adsorption edge of these materials varies from 400 to 520 nm that corresponds to the visible-light energy. Preliminary experiments on the photocatalytic hydrogen production under visible light irradiation were carried out.

References

[1]. V.M. Daskalaki, D.I. Kondarides Catalysis Today 144 **(2009)** 75–80.

Acknowledgements

We gratefully acknowledge the support of the Federal Special Programm “Scientific and Educational Cadres of Innovative Russia” (2009-2013 years).

PP-III-34

PHOTOCATALYTIC WATER PURIFICATION FROM HAZARDOUS ORGANIC COMPOUNDS ON THE SUPPORTED SEMICONDUCTOR CATALYSTS IN THE BATCH REACTORS

Ekaterina Kozlova[1,2], Aleksander Vorontsov[1,2]

[1]Boreskov Institute of Catalysis SB RAS, pr. Ak .Lavrentieva, 5, Novosibirsk, Russia,
kozlova@catalysis.nsk.su
[2]Novosibirsk State University, Pirogova, 2, Novosibirsk, Russia

Nowadays there is a great problem of purification of water from different pollutants. Photocatalytic oxidation in aqueous suspension of cheap and non-toxic semiconductor catalyst titanium dioxide is an effective method for the degradation of organic compounds of many classes. Usually nanosized titania particles are used for the water purification processes. Unfortunately, for applications in aqueous phase such a small particle size is not suitable due to further filtration difficulties. These problems lead to the development of the different supports for the TiO_2 photocatalyst. Usually the oxidation rate falls after the photocatalyst deposition. In this work, we aimed at the photocatalytic oxidation of organophosphorous dimetyl methylphosphonate (DMMP) on Pt/TiO_2 Degussa P25 deposited on glass fiber support. DMMP was chosen as the substrate because it imitates organophosphorous pestisides, for example malathion. We proposed glass fiber fabric as support because it is light, easily formed and cheap material. The specimens of supported photocatalyst were obtained by the impregnation of glass fiber fabric pieces with the mixture, which contain silicagel, with further drying and annealing. Then the photocatalyst 1% Pt/TiO_2 Degussa P25 was deposited by dip-coating technique (Fig. 1).

Figure 1. The glass fiber supports with pure and platinized TiO_2 Degussa P25.

The supported catalyst has shown the stable rate of DMMP oxidation in 10 consecutive experiments. The rate of the oxidation on the supported titania was practically the same as in the photocatalyst suspension. The material for the support preparation (glass fiber fabric) is quite cheap, as well as reagents used for the impregnation mixture preparation. The technique of the support preparation allows one to create different shapes of the support in the stage of silicagel hardening. Therefore, the technique of the photocatalyst support preparation described above is shown to be very prospective. The support has been patented [1].

The next step of our investigation was studying of the photocatalytic oxidation of phenol in the batch recirculating reactor with the total volume of the reaction solution 3 L. The support with the catalyst was made by the same technique as for the experiments with DMMP. The tube-shaped support had several layers. The catalyst 0.2% Pt/TiO_2 Degussa P25 was used in order to decrease the noble metal amount. The body of the photocatalytic reactor is shown in Fig. 2.

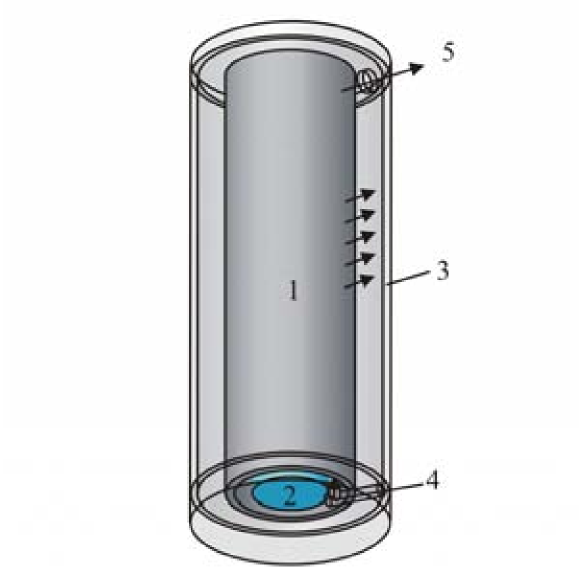


Figure 2. Photocatalytic reactor.
1 – glass fiber based support with the catalyst; 2 – UV-lamp; 3 – outer wall; 4 – reaction mixture inlet; 5 – reaction mixture outlet.

It was shown that the rate of the phenol oxidation on the supported titania is as high as in suspended catalyst. Thus, the proposed support is suitable for the scaled-up reactors. The development of the new glass fiber based supports allows one to make the photocatalytic devices cheaper and easier.

References

[1]. Patent RU 2375112.

Acknowledgements

We gratefully acknowledge the partial support of NATO grant SfP-981461, SB RAS integration grants # 36 and 70, SB RAS Presidium grant # 27.56, Lavrentiev Grant for Young Scientists as well as Russian Science & Innovation Federal Agency (Scientific and Educational Cadres Programm).

PP-III-35

STUDIES ON PHYSICO-CHEMICAL CHARACTERISTICS OF SILVER INDUCED IOTA-CARRAGEENAN EXTRACTED BY ULTRASONIC METHOD

Reddy Prasad D.M.[1], Duduku Krishnaiah[2], Awang Bono[2], Kamatam Krishnaiah[3], Rosli bin Mohd Yunus[1]

[1]Faculty of Chemical & Natural resources Engineering, Universiti Malaysia Pahang, 26300Gambang, Kuantan, Pahang Darul Makmur, MALAYSIA, Tel: +609-5492381, Fax: +609-5492399. dmrprasad@ump.edu.my (or) dmrprasad@gmail.com
[2]School of Engineering and Information Technology, Universiti Malaysia Sabah, Locked Bag No. 2073, 88999 Kota Kinabalu, Sabah, Malaysia
[3]Department of Chemical Engineering, Indian Institute of Technology Madras, Chennai 600 036, India

Extraction is the key processing step for the recovery and purification of active ingredients of plant material. The traditional techniques of solvent extraction of plant materials are mostly based on the appropriate choice of solvents and the use of heat and/or agitation to increase the solubility of components and the rate of mass transfer. Usually, these techniques require long extraction time and have low efficiency. Moreover, many natural products are thermally unstable and may degrade during thermal extraction [1]. The key objective in any extraction procedure is to achieve high extraction efficiency at a reduced processing time. In this respect, a procedure that could yield the highest yield of the effective constituents in a shorter processing time would be the ultrasonic assisted technology [2].A 20 kHz intensity ultrasound was used in the extraction of iota- carrageenan from *Eucheum denticulatum* seaweed by using water as solvent. In a simplified extraction procedure, seaweed particles of 0.7125, 1.2 and 1.7 mm diameter were added to the solvent and ultrasonicated at different ultrasonic amplitude levels, ranging from 2.08 x 10^{-06} m to 6.4 x 10^{-06} m and the temperatures from 30°C to 60°C with 10°C increment. The maximum iota-carrageenan yield obtained was 57.2 %. Particle diameter variation during the extraction was found to be a linear equation. The solid–liquid mass transfer coefficient was correlated for ultrasound extraction of iota-carrageenan in terms of operating conditions employed in this investigation as $K_L = 0.1075\left(A^{0.866}\right)\left(D_p^{-0.533}\right)\left(T^{0.133}\right)$. The study suggests that ultrasound intensity reduced the extraction time required, and improved the yield of iota-carrageenan by 6%.

In the modification process, for polyelectrolytes, counter ions play a major role in the carrageenan gelation process. Some of the cations are reacted and caused for modification of gelation properties in the natural polymers. Besides, few investigations pertaining to the gelling mechanism, focused on the configuration of the initial ordered state of the helices. The gel formation occurred in the presence of K^+, Rb^+, Cs^+ and at high concentrations of Na^+ and a double helix based 'aggregated-domain' structure as the gelled structure was proposed [3]. The aggregation of 'helical dimers' to form a three dimensional network in the presence of potassium, sodium and rubidium was investigated [4]. At high polymer concentration (~ 21.6 g/l), it was found that the elastic modulus was not affected by divalent salt concentration above a certain threshold and also proposed that the addition of cations beyond this critical value contributes only to some localized heterogeneity within the gels without affecting the overall viscoelastic properties of the systems [5]. The existence of an optimum counter-ion concentration in silver-induced iota-carrageenan from ucheuma denticulatum at low polymer concentrations of 1, 1.2 and 1.5 weight percent was observed. The weight loss for gels was found to be in the range 0.7-1.2% and after 240 h with a standard deviation of 0.01-0.2%. The gels exhibited high firmness as the Ag+ concentration increased while decrease in the elasticity was observed. The relaxation time reached maximum at 70 mM of Ag+ and at higher concentration the gels exhibited saturation. Scanning electron microscope images show that the extensive structural charge neutralization of the polysaccharide by monovalent silver ions is responsible for a marked aggregation of the polymer strands reminiscent of precipitation. At lower counter-ion to polymer ratios, the onset of gelation might prevent such phase separation. Results with higher concentrations suggested that the iota- carrageenan gel films exhibited cracks on the surface. It was attributed to the brittleness and lower gel film strength.

Reference:

[1]. Wu, J., Lin, L., & Foo, T.C., Ultrason. Sonochem. 8 (**2001**) 347.
[2]. Xia, T., Shi, S., & Wan, X., J. Food Eng. 74(**2006**) 557.
[3]. Morris, E. R., Rees, D. A., J. Mol. Biol. 138(**1980**) 349.
[4]. Rochas, C., Rinaudo, Biopolymers, 23(**1984**) 735.
[5]. Michel A-S, M.M.Mestdagh, M.A.V.Axelos., Int. J. Biol. Macromol. 21(**1997**) 195.

KINETICS OF HEMICELLULOSES HYDROLYSIS

Bright T. Kusema[1], **Gerd Hilpmann**[1], **Tea Tönnov**[1], **Päivi Mäki-Arvela**[1], **Stefan Willför**[2], **Tapio Salmi**[1], **Dmitry Yu. Murzin**[1]

[1]Laboratory of Industrial Chemistry and Reaction Engineering
[2]Laboratory of Wood and Paper Chemistry
Process Chemistry Centre, Åbo Akademi University, FI-20500 Åbo/Turku, Finland
E-mail: bright.kusema@abo.fi

Polysaccharides derived from various renewable sources have drawn great interest nowadays. The interest is generated by their features such as the ability to produce biodegradable and biocompatible new products as well as value-added chemicals. Arabinogalactans (AG) and galactoglucomanans (GGM) are hemicelluses which are found in large quantities in most softwood species and they account for 15-25 weight % of the dry wood material. The structural basis of AG is a backbone of β-galactopyranosyl residues that are predominantly (1→3) – linked and most frequently branched with D-galactopyranosyl, L-arabinofuranosyl and D-glucuronic acid side chains. The average ratio of galactose, arabinose and glucuronic acid in the AG is about 5:1:0.08. GGM consists of a linear backbone of randomly distributed (1→4)-linked β-D-mannospyranosyl and (1→4)-linked β-D-glucopyranosyl units, with (1→6)-linked α-galactopyranosyl and β-D-galactopyranosyl units as single unit side units. The average ratio of galactose, glucose and mannose in GGM is about 0.5:1:4. The molar mass of AG and GGM is 20 000 – 100 000 g/mol. Extraction of the hemicelluloses can easily be carried out with water at moderate temperetures. GGM can be recovered in industrial scale from process waters in mechanical pulp mills. Therefore AG and GGM has a great potential to serve as a sustainable feedstock for valuable chemicals [1, 2, 3]

The focus of this research is to convert AG and GGM into valuable products through a sugar platform which includes two processes: hydrolysis of the hemicellulose to monomers and catalytic transformation of the monomers into bio-based valuable products. The topic is timely as hydrolysis of plant-derived polysaccharides to platform sugars in good yields is an increasingly important issue. AG and GGM have direct medical applications as health products. In foods, they are used as stabilizer, emulsifier, binder and sweetner. The monomers have applications as specialty sugars in the food, pharmaceutical and cosmetic industries [4, 5].

The kinetics of acid hydrolysis of AG and GGM was studied isothermally in a batch reactor. A number of homogenous acids such as hydrocloric acid (HCl), sulphuric acic (H_2SO_4) and trifluoroacetic acid (TFA) were tested and their effects on the rates compared. The main reaction parameters were the acid concentration (pH=1-3), temperatures up to 100°C and substrate concentrations. The hydrolysis rates increased with the acid concentration (pH) and temperature. Complete hydrolysis of AG and GGM was achieved without any further degradation of the monomers. The activities of acidic heterogenous catalysts such as ion exchange resins and zeolites were also elucidated. Their application in biomass hydrolysis is inline with green chemistry approach in the development of novel technologies.

References

[1]. Willför, S.; Holmbom, B. “Isolation and characterization of water-soluble polysaccharides from Norway spruce and Scots pine”, J. Wood. Sci. Technol., **2004,** 38, 173–179.

[2]. Xu, C.; Pranovich, A.; Vähäsalo, L.; Hemming, J.; Holmbom, B.; Schols, H.; Willför, S. “Kinetics of acid hydrolysis of water-soluble spruce O-acetyl galactoglucomannans”, J. Agric. Food Chem., **2008,** 56, 2429-2435.

[3]. Kusema, B.; Xu, C.; Mäki-Arvela, P.; Willför, S.; Holmbom, B.; Salmi, T.; and Murzin, D. "Kinetics of acid hydrolysis of arabinogalactans", I. J. Chem. Reactor Eng., **2010,** Vol. 8, 1.

[4]. Kelly, G.; “Larch Arabinogalactan:Clinical relevance of a novel immune-enhancing polysaccharide”, **1999**, Altern. Med. Rev. 4, 96-103.

[5]. Willför, S.; Sundberg, K.; Tenkanen, M.; Holmbom, B. “Spruce derived mannans – a potential raw material for hydrocolloids and novel advanced natural materials”. Carbohydr. Polym., **2008**, 10.1016/j.carbopol.2007.08.006.

Acknowledgements

This work is part of the activities of the Process Chemistry Centre (PCC) at Åbo Akademi University within the Finnish Centre of Excellence Programme (2006-2011) by the Academy of Finland.

PP-III-37

BENZALDEHYDE REDUCTION OVER IRON AND MANGANESE MESOPOROUS MOLECULAR SIEVES CATALYSTS

Kahina Lanasri[1], Khaldoun Bachari[1,2], Djamila Halliche[1], and Adel Saadi[1]

[1]Laboratoire de Chimie du Gaz Naturel, Faculty of chemistry, USTHB, BP32 El-Alia,
16111 Bab-Ezzouar, Algeria. E-mail address: adel_saadi@yahoo.fr
[2]Centre de Recherche Scientifique et Technique en Analyses Physico-Chimiques.
BP 248, 16004 Algiers, Algeria

Aromatic compounds, with preferred functional groups are key in chemical industries, as they are intermediates for the manufacture of dye stuffs, pharmaceutical, agricultural and photographic chemicals, additives, surfactants textile auxiliaries, chelating agents, and polymers [1]. Aromatic alcohols are generally prepared by reduction of aromatic aldehydes, mostly by reduction with metals. In the present study, we report the results obtained in the gas phase reduction of benzaldehyde over iron-HMS-n and manganese-HMS-n (n=50, 25, 15) catalysts.

The catalysts were prepared using a protocol reported by Tanev et al. [2] and the resulting precursors were dried at 100°C and calcined in air (350°C/3h). The solids were characterized by their BET specific area, XRDiffraction and IRFT spectroscopy. The catalytic reactions were carried out in a fixed bed glass reactor with 0.2g samples at atmospheric pressure and in the temperature range: 100°C-250°C (H_2 per-reduction: 350°C).

The specific area of the catalysts decreased with the metal loading and was in the range of 800–1120 m^2g^{-1}. The XRD spectra showed the characteristic bands of the HMS material and metal. The intensity of the peak decreased when the nickel content increased showing that the addition of nickel has a negative effect on the crystallinity. The FTIR spectra of the solids showed three peaks: the first peak is attributed to the symmetrical Si-O-Si stretching vibration, the second is assigned to symmetric stretching vibration of Si-O-M (Fe and Mn), and the third, is attributed to SiO_2 harmonic.

As a general trend, the benzaldehyde reduction results showed that the steady-state conversion increased with reaction temperature (120-240°C) for all catalysts and on the other hand, the activity increased with the metal loading catalysts. The reaction products were toluene and benzene. They resulted from two types of reaction: i) C=O double bond reduction to toluene; ii) C-C exocyclic bond hydrogenolysis to benzene.

Fe-HMS and Mn-HMS catalysts does not formed benzylalcohol product. Toluene appeared as a low reaction temperature product rather favoured on Fe-HMS and Mn-HMS catalysts (30%-60% of selectivity). Benzene was formed at high reaction temperature (40%-70%), preferentially on the Fe-HMS catalyst. No cyclohexane was detected indicating a high stability of benzene in the reaction conditions used.

References

[1]. A. Rahman, S.B. Jonnalagadda, J. Mol. Catal. A : Chemical 299 **(2009)** 98-101.
[2]. P.T. Tanev, M. Chibwe, T.J. Pinnavaia, Nature 368 **(1994)** 317.

LOW-TEMPERATURE REFORMING OF ETHANOL OVER NICKEL-COPPER CATALYST

Lapin N.V., Bezhok V.S.

Institution of Russian Academy of Sciences
Institute of Microelectronic Technology and High-Purity Materials, RAS,
Chernogolovka, Russia. Fax: (495)962-8047, E-mail: lapin@iptm.ru

Hydrogen is promising fuel for various power plants, low-power devices (1-50W) included [1]. The latter can be portable fuel cells and charging units to energize notebooks, cell phones, etc. However, accumulation and storage of molecular hydrogen nowadays present a problem because of safety concerns during hydrogen capacitors exploitation and their small capacitance to hydrogen. One of possible pathways to overcome the difficulties can be hydrogen production from hydrocarbons, e.g. alcohols (methanol or ethanol), by water-vapor catalytic conversion. In this case ethanol has a number of advantages over methanol such as low cost, low toxicity, ease of transporting, exploitation, and production from renewable sources (bioethanol). When hydrogen is used to supply portable fuel cells, integration of a fuel cell and a fuel microchannel converter seems most perspective [2]. In this case, the catalyst should be placed on the channel walls, where highly developed catalyst surface can hardly be obtained. In this work we studied low-temperature steam reforming of ethanol over a bimetal nickel-copper catalyst deposited onto a quartz fiber of small specific surface.

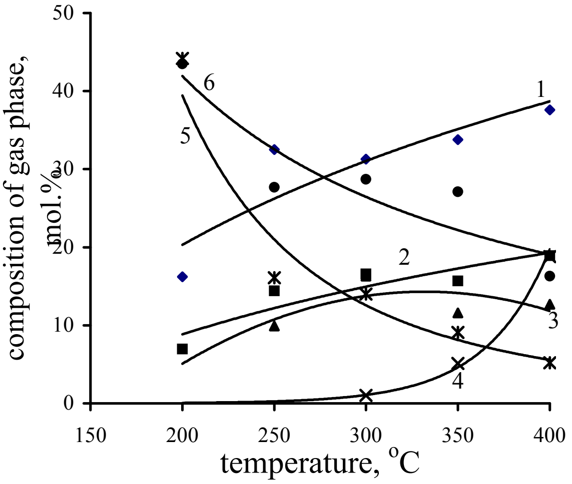


Fig.1. Temperature dependence of the gas phase composition during the conversion of ethanol and water: 1 – hydrogen, 2 – methane, 3 – carbon monoxide, 4 – carbon dioxide, 5 – ethanol, 6 – water.

The catalyst was prepared by impregnation quartz fibers in water solution of nickel and copper nitrates of corresponding quantities. The catalyst charge (without the support) was 0,4g, with the copper content in the catalyst 15 wt %.

Ethanol-water molar ratio was 1:1,2. It was shown earlier [3] that the main products of ethanol-water mixtures reforming over a nickel catalyst are hydrogen, methane and carbon monoxide. All these products are present approximately in equal amounts (one third of the total gas phase) in the whole range of temperatures studied (200-400°C). Small amounts of acetaldehyde, as a product of ethanol dehydrogenization, were observed. It was noted that water is not involved in the process, which points to the absence of the shift-reaction, i.e. the process is a catalytic pyrolysis of ethanol. The results of this investigation of ethanol-water reforming over the nickel-copper bimetal catalyst are presented in Fig.1. It is seen that the major products of reforming are hydrogen, methane, carbon monoxide and carbon dioxide. The conversion of ethanol starts at 200°C and completes almost by 90% at 350°C. As the conversion proceeds, the concentration of all products increases. The concentration ratio of hydrogen, methane and carbon monoxide remains constant, with the hydrogen concentration being twice as high as those of methane and carbon monoxide. At 300°C carbon dioxide appears in the gas phase, its content increases abruptly at 350°C and makes 20 mol% at 400°C. At this temperature, the carbon monoxide concentration reaches the maximum and then drops to 10 mol%, evidently due to the shift-reaction and carbon monoxide disproportionation. The selectivity of hydrogen and methane slightly decreases (by 10-15%) as the temperature rises because of an increase of CO_2 content in the gas phase; the selectivity of carbon monoxide reaches the maximum at 350°C. At temperature below 300°C, the selectivity of carbon dioxide is low but increases abruptly with temperature. The results obtained suggest that the resistance to diffusion exerts no appreciable effect on mass transfer in the gas phase. Also the conversion of the ethanol-water mixture should produce 2 moles of hydrogen per 1 mole of ethanol. In fact, only 1 mole of hydrogen is produced directly from ethanol, the other is obtained from water as a result of shift-reaction and, partially, from water-vapor conversion of methane. These suggestions are supported by the literature thermodynamic calculations which show that the equilibrium constants of these reactions in the studied temperature range are fairly large.

References

[1]. Haryanto A., Fernando S., Murali N., Adhikari S. Current status of hydrogen production techniques by steam reforming of ethanol: a review // Energy & Fuel. 2005. V.19. P. 2098-2106.

[2]. Pattekar A.V., Kothare M.V. A microreactor for hydrogen production in micro fuel cell applications // IEEE J. of Microelectromechanical systems. 2004. V.13. No1. P. 7-18.

[3]. Lapin N.V., Red`kin A.N., Bezhok V.S., Vyatkin A.F. Hydrogen production by catalytic pyrolysis of ethanol over a nickel catalyst. Russian Journal of Physical Chemistry A, 2009, Vol.83, No11, pp.1855-1859.

HYDRODECHLORINATION OF TRICHLOROETHYLENE IN MEMBRANE REACTOR WITH Pd-LOADED POLYPROPYLENE HOLLOW FIBERS

Lebedeva V.I., **Tereshchenko G.F.**[†], **Basov N.L.**, **Petrova I.V.**, **Volkov V.V.**

A.V. Topchiev Institute of Petrochemical Synthesis RAS, Moscow, Russia,
lebedeva@ips.ac.ru

Because of many chlorinated organics are known of potential to public and the environment, so there is an urgent need to develop effective treatment methods. Trichloroethylene is considered one of the most common hazardous organic contaminants found in groundwater. Chemical treatment by catalytic hydrodechlorination is a convenient and promising method for decontamination of organohelogen waste and contaminated water. A wide variety of hydrogechlorination reaction system have recently appeared in the literature, among them catalysis systems with are usually performed with transition metal catalysts (Pd, Pt) and hydrogen sources (H_2, formic acid, hydrazine, metalhydrides) with the advent of accessible methods for the preparation nanometal particles [1,2]. Nanoparticles Pd are higtly effective catalyst for the removal (hydrogechlorination) trichloroethylene [TCE] in groundwater. The nanoparticles provide the maximum number of Pd atoms and greatly improve the efficiency of process several orders of magnitude over bulk palladium catalyst.

In this work hydrogechlorination TCE in water was studied in a static membrane reactor with Pd-loaded polypropylene (PP) hydrophobic porous hollow fiber at ambient temperature. Catalytic nanoparticles Pd have been immobilized on the outer surface PP porous hollow fiber, by method of reduction of palladium salts by aliphatic alcohol [3]. In membrane reactor water with dissolved TCE is contacting with catalytic side PP fibers, but does not penetrate into pores, and hydrogen is fed inside the hollow fibers and diffuses through pores to the outer Pd-coated of fibers [4]. Dissolved oxygen in water has no negative effects on the hydrodechlorination TCE rate, because removal dissolved oxygen from water and reaction hydrodechlorination TCE is passed simultaneously (at the same time).

Transformation of TCE yielded ethane as the main reaction product. Minor amounts of ethylene were formed, but a correlation ethane/ethylene was changed from 25 to 60, which was depended on charge velocity H_2. As a result of the hydrodechlorination TCE HCl produced pH decreased from initial value of 6.5-6.8 to 2-3. Regeneration Pd catalyst is not necessary, because HCl produced as a byproduct in the hydrodechlorination TCE does not decrease Pd catalyst activity, which was constant during the course of 50 h.

References

[1]. Lowry G.V., Reinhard M., Environ. Sci. Technol., **1999**, 33, 1905-1910.
[2]. Fritsh D., Kuhr K., Mackenzie K., Kopinke F.D., Catal. Today, **2003**, 82, 105-108.
[3]. Lebedeva V.I., Gryaznov V.M., Petrova I.V., Volkov V.V., Tereshchenko G.F., Shkolnikov E.I., Plyasova L.M., Kochubey D.I., van der Vaart R., Kinetics and Catalysis, **2006**, 47, 6, 867-872.
[4]. Van der Vaart R., Lebedeva V.I., Petrova I.V., Plyasova L.M., Rudina N.A., Kochubey D.I., Tereshchenko G.F., Volkov V.V., van Erkel J., J. Membr. Sci., **2007**, 299, 38-44.

EFFECT OF Pd ADDITION TO Cu-Zn/CeO_2-ZrO_2 CATALYTIC MONOLITHS FOR HYDROGEN PRODUCTION BY DME STEAM REFORMING

Cristian Ledesma, **Jordi Llorca**

Institut de Tècniques Energètiques, Universitat Politècnica de Catalunya
Av. Diagonal 647, Ed. ETSEIB, 08028 Barcelona, SPAIN
Fax: (0034)934017149, E-mail: jordi.llorca@upc.edu

Introduction

Fuel cells are currently considered as a high efficient technology and clean power generators for both mobile and stationary applications [1]. The production of hydrogen via reforming of various fuels like bioethanol or dimethyl ether (DME) has been regarded as one of the most efficient processes for deployment of fuel cell systems [2].

DME can be obtained from biomass as a raw material via gasification processes and has a high hydrogen to carbon ratio and high energy density. Moreover, DME is corrosion-safe, nontoxic and safe for handling, storing and transportation [1-3].

DME steam reforming comprises two consecutive reactions: DME hydrolysis catalyzed by solid acids and methanol steam reforming over Cu, Zn or Pd-based catalyst. The overall reaction is (1):

$$(CH_3)_2O + 3\ H_2O \rightarrow 6\ H_2 + 2\ CO_2 \quad \Delta H^o = 135\ \text{kJ mol}^{-1} \qquad (1)$$

Literature provides several examples of powder catalysts with formulations containing both acidic and metal sites but only a few examples using catalytic monoliths have been described for this process [1-4].

Our group studied recently the performance of catalytic monoliths containing Cu-Zn/CeO_2-ZrO_2 for DME steam reforming [5]. In this work, a 1% of Pd is added to those catalysts and their performance for DME steam reforming is reported.

Catalysts preparation

Cordierite monoliths were first coated with 10% w/w of ZrO_2, CeO_2 and $Ce_{0.5}Zr_{0.5}O_2$ supports, using zirconium oxychloride and cerium trichloride as precursors. Monoliths were dried under continuous rotation at 373 K for 2 h and calcined in air at 773 K for 2 h. Mixtures of Cu-Pd, Zn-Pd and Cu-Zn-Pd were then added to each support by incipient wetness impregnation using copper, palladium and zinc nitrates as precursors. The metal loading was 10% w/w for Cu or Zn and

1% w/w for Pd with respect to the support. The resulting catalytic monoliths were dried under continuous rotation at 373 K for 2 h and calcined in air at 773 K for 5 h.

Catalysts characterization

X-ray diffraction has been used to study the possibility of alloy formation between Cu-Zn, Cu-Pd or Zn-Pd. The surface composition of the catalysts has been determined by X-ray photoelectron spectroscopy.

Catalytic tests

DME steam reforming has been carried out at atmospheric pressure using a conventional flow reactor (20 mm ID). Prior to reaction, catalytic monoliths have been activated at 573 K with a 10% H_2/N_2 mixture for 1 h. A DME:H_2O=1:3 (molar) gaseous mixture balanced in N_2 has been passed through the reactor at 473-723 K under a GHSV of 1300 h^{-1}. DME steam reforming has also been studied without N_2 dilution with a liquid pump. Reactants and products have been analyzed on-line continuously with a gas micro-chromatograph. It is deduced that the activity of the catalysts increases due to Pd addition; however, the yield of hydrogen, the CO_2/CO ratio and the presence of by-products is strongly influenced by the different catalyst formulation tested.

References

[1]. K. Faungnawakij, Y. Tanaka, N. Shimoda, T. Fukunaga, S. Kawashima, R. Kikuchi, K. Eguchi; *Appl. Catal. A: Gen.*, **2006**, 304, 40-48.

[2]. S. D. Badmaev, P. V. Snytnikov; *Int. J. Hydrogen Energy*, **2008**, 33, 3026-3030.

[3]. T. Mathew, Y. Yamada, A. Ueda, H. Shioyama, T. Kobayashi, C. S. Gopinath, *Appl. Catal. A: Gen.*, **2006**, 300, 58-66.

[4]. M. Nilsson, K. Jansson, P. Jozsa, L. J. Pettersson; *Appl. Catal. B: Environ.*, **2009**, 86, 18-26.

[5]. C. Ledesma, J. Llorca; *Chem. Eng. J. (Amsterdam, Neth.)*, **2009**, 154(1-3), 281-286.

Acknowledgements

Financial support from MICINN through grant CTQ2009-12520 is acknowledged.

PLASMACATALYTIC REACTOR FOR PRODUCING ACTIVE CARBON FROM NATURAL GAS

Makarov A.A.[1], Makarov M.A.[1], Makarov A.M.[1], Trushkov J.J.[2]

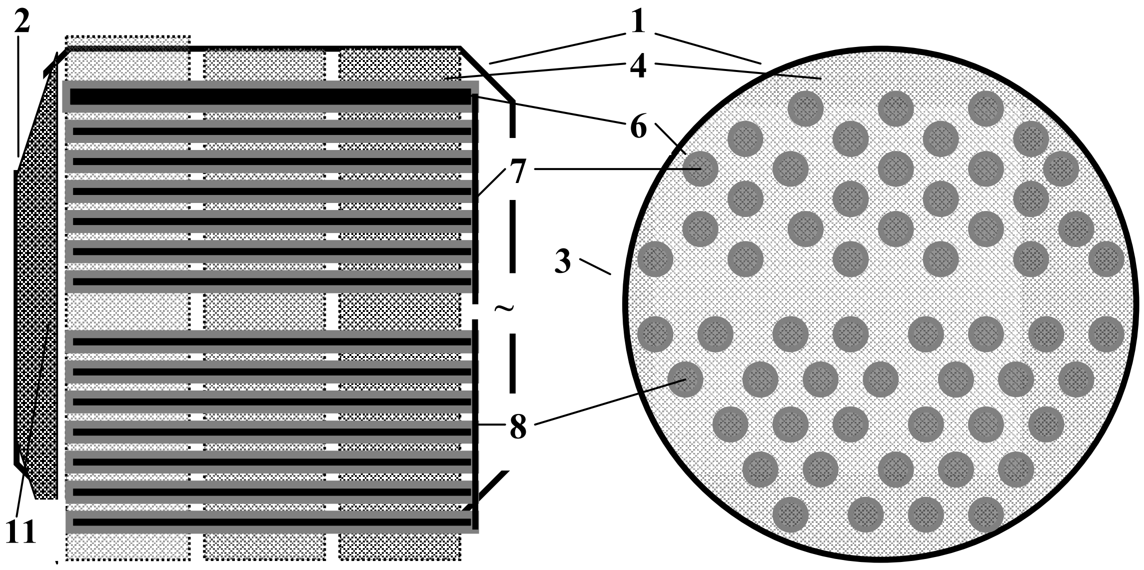
[1]ZAO ECAT, Perm, Russia, mak_perm@mail.ru
[2]Perm state technical university, Perm, Russia

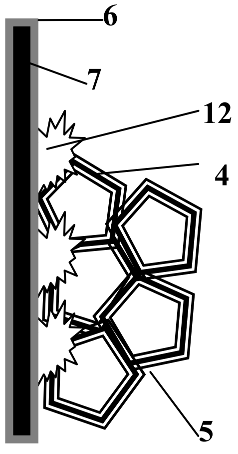
A plasma-and-chemical reactor for the treatment of natural combustible gases, flue gases consists of an input channel with a metal mesh filter and an output channel between which a power supply unit, a gas discharge assembly made in the form of the plasma generator, a catalyst chamber and a fan with a control unit are located.

The gas discharge assembly made as the plasma generator consists of an isolation cassette with a set of plates made of high-porous honeycombed material (HPHM), a dielectric and an electroconductive plate. The catalyst chamber includes a heat- and gas-insulated partition; heating elements fixed on HPHM catalytic elements made of metal HPHMs of the chamber; catalytic elements made of high-porous honeycombed materials and fastenings for heating elements.

The power supply unit (the impulse high voltage power source) is constructed according to the power-bridge transformer circuit. The basic inductive element, i.e. the transformer, operates in the transit mode and does not save any magnetic power. It operates in symmetrical mode at low excitation currents. Due to this, such a transformer has smaller dimensions with the same capacity; its calculations are easier. Low excitation current means less quantity of power accumulated in the leakage inductance. Hence, its suppression does not require complex damping circuits and switching-over processes in the transformer are considerably “quieter”.

The high-porous honeycombed material permeable for the medium being purified is used as a discharge electrode. It is connected to one pole of the power supply; the other pole is connected to the electroconductive plate on the opposite side of the dielectric. The channel length is restricted by the distance between the HPHM cells. The number of micro-discharges increases proportionally to the voltage growth. Thus their density increases which results in more effective use of the surface and more power in the discharge area. The gas flow that passes through the permeable HPHM electrode is turbilized, interacting with the chaotic porous structure of the electrode material. Besides, the molecules of natural gas are destroyed both the discharge low-temperature plasma. HPHM electrode also serves as collecting self-regeneration gas filter. Due to impact intercepting procedure the most fine-dyspersated particles, including the soot ones are deposited and aggregated on the plates. Free radical reactions of destruction of organic compounds in the gaseous phase which began in the gas mixture continue after the air passes the partition on the highly-developed HPHM surface with catalytic cover based on aluminum and rare-earth metal oxides.





A MEDIUM-POWERED MICROCHANNEL FUEL PROCESSOR FOR THE GENERATION OF SYNTHESIS GAS DURING METHANE PARTIAL OXIDATION

Makarshin L.L., Andreev D.V., Gribovskyi A.G., Sadykov V.A., Mezentseva N.V. and Parmon V.N.

Boreskov Institute of Catalysis SB RAS, 630090 Novosibirsk, Russia
Novosibirsk State University, Novosibirsk, Russia
makarshin@catalysis.ru

The development, investigation and testing of fuel processors integrating different reactors and systems provide the performance of continuous generation of synthesis gas [1]. We developed and tested a compact fuel processor producing synthesis gas from light hydrocarbons.

The processor involves 6 particularized microchannel reactors, 4 microchannel heat exchangers integrated with mixers and 2 evaporators. Prior to assembling of the fuel cell, we tested microchannel reactors.

The testing results are: microreactor 1 for the complete methane oxidation (volume 3.7 cm^3, 20 microchannel plates) provided 486 W of thermal energy at 100% conversion of methane. Microreactor 2 for the partial methane oxidation (size 25x25x6 mm, 30 microchannel plates) generated 380 l/h of hydrogen at a 100% conversion of methane and a reaction temperature of 820°C. Consequently, the maximal heat energy with respect to hydrogen was ~1000 W. The subsequent cleaning of synthesis gas from carbon monoxide was performed in microreactors 3 and 4 during high-temperature (350°C) and low-temperature (210°C) steam reactions. The resulting gas mixture involved: H_2 34,7%, CH_4 1.2% N_2 44.5%. CO 1.5% CO, and CO_2 18.1%. Fine cleaning of synthesis gas from carbon monoxide was performed in microreactors 5 and 6 during high temperature (200°C) and low-temperature (150°C) selective oxidation of carbon monoxide by air oxygen. At the outlet from reactor 6, the concentration of carbon monoxide was reduced to 20 ppm, which is sufficient for feeding a fuel cell with a polymer membrane.

The assembling of the fuel cell, calculations of the heat balance and preliminary tests of the model showed that the maximal efficiency (63%) of the cell can be achieved at an input methane flow rate of ~ 95 l/h.

In this case, the specific heat output of the fuel cell was 550 W/dm^3. The limiting stage is the reaction of water gas and the selective oxidation of carbon monoxide.

References

[1]. Promising Energy Technologies on the Earth and in Space, Collected works under the editorship of A.S. Koroteyev, Moscow, 2008 (in Russian).

METHANOL AND DIMETHYL ETHER SYNTHESIS IN SUPERCRITICAL CONDITIONS OVER (Au, Ag) – Cu/$ZnAl_2O_4$ CATALYSTS

Paweł Mierczyński, Tomasz P. Maniecki, Katarzyna Bawolak,
Wojciech K. Jozwiak

Technical University of Lodz, Institute of General and Ecological Chemistry
90-924 Lodz, Zeromskiego 116, e-mail tmanieck@.p.lodz.pl

Methanol and DME synthesis in supercritical conditions is an interesting opportunity to the classical industrial process. During last years a few rapports referring to this method of oxygenate production can be found in the literature. Synthesis in supercritical conditions allows to achieve a mixture of CH_3OH and $(CH_3)_2O$. The product distribution depends strongly from catalysts and reaction conditions (pressure, temperature, kind of supercritical fluid). Such mixture can be directly used as a fuel for diesel engines (for DME cetane number – 55, petroleum achieves 53 only). Additionally European Union consider the possibility of use DME as primary fuel for diesel engines in 2030. Above mentioned facts suggest that new ways of methanol and DME synthesis are necessary. For both process a typical methanol synthesis catalysts can be used.

In this work we studied the influence of catalyst composition and, reaction conditions on selectivity and yield of oxygenates synthesis.

Catalysts were prepared by coprecipitation method from zinc, aluminum and copper nitrates. Mixture of hydroxides were dried and finally calcined at 400C. Promoters (Au, Ag) were introduced by impregnation or precipitation method. Copper content was 10-60%$_{wt}$, Promoters content was 1 or 5% of weight. Prior to reaction catalysts were reduced in 5%H_2-95%Ar mixture. Reaction were carried out in a system built on the base of small autoclave, high pressure flow regulators and back pressure regulators. Liquid phase used as a supercritical solvent were introduced via hplc pump. Synthesis were carried out in a $CO/CO_2/H_2$ feed with molar ratio 4:2:12. As a supercritical fluid we used n-pentane or n-octane. The reaction pressure had a strong influence on reaction way. In low pressure range DME as a main reaction product were observed. At higher pressure (above 100 bar) methanol was the main product of reaction. The CO conversion achieve 50% for the most active catalyst. The most active was catalyst 20%Cu-1%Au/$ZnAl_2O_4$.

DEVELOPMENT OF AN INTEGRATED SEPARATOR FOR DIRECT REFORMING OF HYDROCARBONS IN HIGH-TEMPERATURE FUEL CELLS

Mishanin S.V.[1], **Malinov V.I.**[1], **Ismagilov Z.R.**[2], **Kerzhentsev M.A.**[2],
Podyacheva O.Yu.[2], **Ulyanitskiy V.Yu.**[3], **Mitina L.M.**[4]

[1] *Russian Federal Nuclear Center – All-Russian Scientific Research Institute of Experimental Physics, Sarov, Russia; mishanin@astra.vniief.ru*
[2]*Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia*
[3]*Lavrentiev Institute of Hydrodynamics, Pr. Lavrentieva, 15, Novosibirsk, Russia*
[4]*International Science and Technology Center, Moscow, Russia*

Fuel cells are electrochemical reactors which directly convert chemically stored energy into electrical energy at high thermodynamic efficiencies.

Most fuel cell power plants (FCPP) use methane as a fuel which is reformed in a catalytic fuel conditioning system and converted into a gas enriched with hydrogen to be used in a fuel cell stack (FCS) for the electrochemical oxidation reaction.

Methane steam reforming is the most well studied, efficient and most widely used method of hydrogen production in the fuel cell based power plants.

In most FCPPs, catalytic steam reforming is performed in separate fuel processors. The fuel processor is a chemical reactor which requires heat supply to function. As a heat source, natural gas with addition of the FCS products is generally used, i.e. gas mixtures containing a certain amount of combustible components, such as H_2, CO and CH_4. In [1] various schemes of integrated fuel processors for fuel cell application are reviewed. The most efficient schemes are those of internal reforming, which is attractive from the perspective of increased system compactness and efficiency, faster loading response and significant cost reduction. Direct addition of a reforming catalyst into the anode material is proposed for solid oxide fuel cells (SOFC) [2], and an integration of a reforming catalyst separated from the hot anode by a heat conducting wall is proposed for SOFC and molten carbonate fuel cells [3].

One of the most most important elements of the FCS which distributes the fuel and the oxidizer flows in the FC anode and cathode zones and provides electric coupling of cells is a separator (in planar SOFC – interconnector). The separator/interconnector is a plate profiled from a flat metal sheet, where channels for distribution of gas flows are formed (Fig. 1.).

The goal of this work is development of an integrated separator/interconnector for direct reforming of hydrocarbons in high-temperature MCFC and planar SOFC. This goal is attained by using a multi-layer coating on the separator/interconnector. The coating has at least two layers. The first protecive layer (possibly with a sub-layer) has a high degree of adhesion to the metal surface, has a thickness of 25-30 microns and is prepared from metal oxides and/or intermetallides. The second porous catalytic layer has the thickness of at least 100 microns, and contains metals or metal oxides active in methane steam reforming.

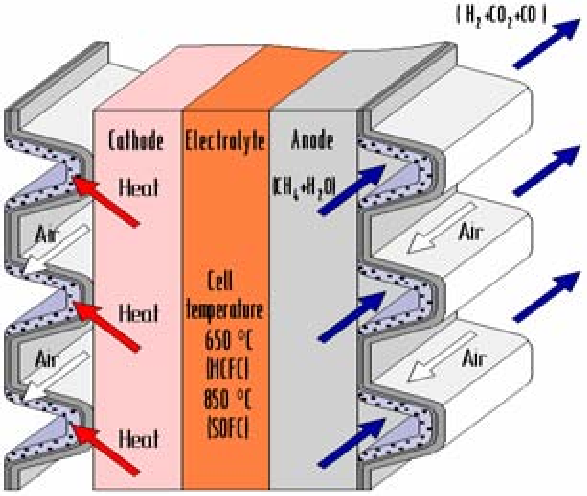


Fig. 1. Schematic diagram of the integrated separator/interconnector operation.

Methods of deposition of powders on metal surfaces for production of integrated separators/interconnectors by plasma spraying, detonation and cold gas-dynamic spraying techniques were developed and tested.

The optimization of the heat balance in small reactor systems of a planar type for reforming of gaseous hydrocarbons in FCPP was performed. A geometrical 3D model of an integral separator/interconnector was developed with a description of physical properties of its elements and its environment. Modeling of the dynamics of heat processes in the integral separator/interconnector during its exploitation was performed using ANSYS software. The calculation of unsteady state heat fields in the 3D layerwise model was carried out taking into account different boundary conditions and assignment of different properties of construction materials and surrounding components in the form of functional dependences. Parametrical optimization of the reactor with the integrated separator/interconnector was done with the output of the results in the interactive, color and graphical forms.

References

[1]. Aidu Qi, Brant Peppley, Kunal Karan, Fuel Processing Technology 88 (2007) 3–22.
[2]. US Patent No 6051329.
[3]. US Patent No 4877693.

Acknowledgements

This work is supported by ISTC, project # 3140.2 and SB RAS Integration Project # 82.

PP-III-45

REACTOR FOR THE DEPOLYMERISATION OF OLIGOLACTIC ACID

Mulyashov S.A., **Sirovski F.S.**, **Beksaev S.G.**, **Kolbakov V.V.**

OU Nordbiochem, Estonia, e-mail: lab-tos@mail.ru

Currently polylactic acid (PLA) is one of the most promising biodegradable polymers due to the unique set of its valuable performance properties. PLA is manufactured from lactic acid obtained by microbial carbohydrate waste fermentation. Unfortunately, the wide use of PLA i.e. for packaging is restricted by higher production costs as compared to polythene, etc.

PLA is obtained by the following reaction chain: lactic acid → oligolactate → cyclic dimer (lactide) → polylactide. The contribution of the lactide synthesis step to the overall production costs is quite significant. Depolymerisation is the most crucial step in lactide synthesis. Increasing the process temperature to 250 °C shifts the oligomer – monomer equilibrium to the right as desired, however the rate of side reactions such as racemisation, dehydration and thermal degradation is significantly increased above 210 °C. These side reactions decrease the quality of the finished product. The issue could be resolved intensifying heat and mass transfer and decreasing reactant residence time at high temperatures.

This could be achieved by carrying out depolymerisation in the vacuum evaporator with the low temperature evaporation zone. Melted oligomer with the temperature ≤210 °C is fed into the tubular heater where its temperature is briefly raised to 220-260 °C. Then it flows into the low temperature evaporation zone. The sharp pressure drop results in intensive lactide evaporation and its efficient removal. The simulation of the process allowed us to calculate the heater, reactant residence time and lactide concentration in the melt prior to evaporation. The real experiments were run on a pilot plant and optimal operation parameters were determined.

OLIGOMERISATION OF TERTIARY AMINE LACTATES

Mulyashov S.A., Sirovski F.S., Beksaev S.G., Kolbakov V.V.

Nordbiochem Ltd., Põlva, Estonia, sbeksaev@inbox.ru

The amount of polymer waste in urban areas is growing at a threatening rate. Incineration of these wastes at municipal incinerating plants generates new risks such as dioxin and other ecotoxicant emission. Thus, biodegradable polymeric materials with a short life cycle became lately the subject of interest. Polylactic acid (PLA) is the most promising of these polymers due to its properties and renewable feedstock. All known methods of PLA manufacture include the microbial synthesis of L-lactic acid as the first step. The next step is a polycondensation to oligomer.

The removal of L-lactic acid from the culture fluid and its subsequent purification presents an important task. Three known methods exist: transfer into calcium lactate, esterification by C_1-C_5 alcohols and as tertiary amine salt. The last method is the most advantageous as there are no solid wastes as in case of calcium and no evaporation of large volumes of water and product distillation is required as in case of esters. Tertiary amines could be recovered and recycled back to the front end.

Lactates of tertiary amines are able to undergo polycondensation affording the oligomer and free amine. It makes possible to use these lactates directly in PLA manufacture.

In this work we studied oligomerisation of trialkylammonium lactates at temperatures between 80 – 240 °C under vacuum. The reaction was monitored by HPLC with UV-detector and GC-MS. We identified several oligomers with n=1-4 and quantified them. The experimental composition of the reaction mixture was compared with theory data.

The flowchart for the production of PLA oligomer using trioctyl amine was developed. The process mass balance and optimal performance parameters for the synthesis of oligomer with molecular mass 1,500-2,000 DA were determined on the existing pilot plant.

PP-III-47

PERFORMANCE OF PHOTOCATALYST FOR PURIFICATION OF RE-FLOW FURNACE EXHAUST GAS

Ryoko Nakano[1], **Eiko Obuchi**[2], **Katsumi Kato**[2], **Katsuyuki Nakano**[1]

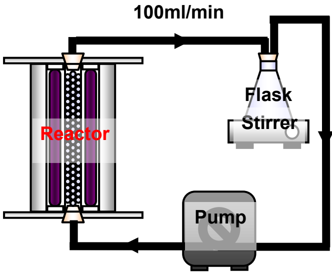
[1]Department of Energy and Environment Systems Faculty of Engineering,
Fukuoka University, Fukuoka University 8-19-1 Nanakuma, Jonan-ku,
Fukuoka 814-0180, Japan, td095503@cis.fukuoka-u.ac.jp
[2]Department of Chemical Engineering, Fukuoka University
8-19-1 Nanakuma, Jonan-ku, Fukuoka 814-0180, Japan

INTRODUCTION

The RoHS (Restriction of Hazardous Substances) has been enforced in EU since July 1, 2006. Due to this enforcement, 6 substances including lead are subjected to this regulation. It is more common to use lead-free solder rather than using solder containing lead these days. The melting point of lead-free solder is 220° which is higher than lead-containing solder (mp: 183°). Thus the re-flow furnace needs to be controlled at high temperature (around 240°) when using lead-free solder. However, there might be a possibility of generation of hazardous substances such as organic nitrogen compounds from the furnace when it is controlled at such high temperature. To solve these problems, Yasukawa Ltd. has developed “Scavenger” as a novel exhaust gas treatment device for re-flow furnace. It takes in the exhaust gas from re-flow furnace and the (harmful) organic compounds in the exhaust gas are absorbed in the nano-bubble water.

The purpose of our research is to purify the waste water by using TiO_2 photocatalytic ceramic filter. At the initial stage of this research, we have investigated the characteristic degradability of organic compounds in the wastewater by using titania photocatalyst supported on silica beads.

EXPERIMANTAL



Experimental conditions
Light source:
Black Light
(6W×4, 3.52mW/cm^2)
Germicidal Light
(6W×4, 5.38mW/cm^2)
Reactor size : H270×i.d.10mm

Fig. 1 Diagram of the experimental apparatus.

Figure 1 shows a diagram of the laboratory scale experimental apparatus. TiO_2/SiO_2 photocatalyst beads were filled in the tubelar reactor and the waste water (C_0:20ppm) was circulated at a flow rate of 100ml/min. After adsorption has equilibrated, 6W×4 black lights (BL) or 6W×4 germicidal lights (GL) were irradiated on the surface of catalyst[1]. Analysis of organic compounds in wastewater was conducted using TOC meter (Shimazu Co.; TOC-5000). Qualitative/quantitative analysis of compounds in wastewater was conducted using GC/MS (HEWLETT PACKARD: HP5973MSD).

RESULTS AND DISCUSSION

Table 1 Change in the reaction rate constant k [min^{-1}]

	BL	BL+TiO_2/SiO_2	GL	GL+TiO_2/SiO_2
Reaction rate constant k [min^{-1}]	0.0007	0.0032	0.0007	0.0044

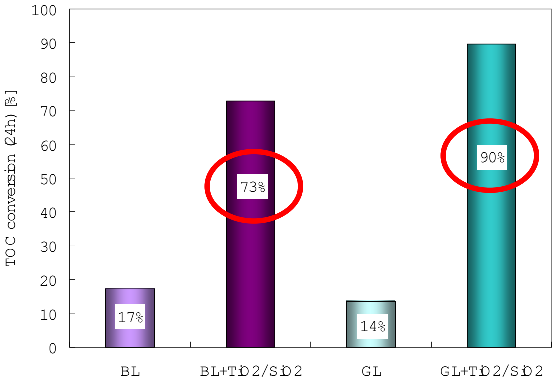


Fig.2 Change in the TOC conversion

The results of experiment were shown in Table1 and Figure 2. There was no photodegradable effect with organic compounds under irradiation by BL and GL without photocatalyst. On the other hand, photodegradation of organic compounds was observed on using TiO_2/SiO_2 and UV light simultaneously. Comparing the kinds of light, both first order reaction rate constant and TOC conversion after 24 hours of above experiment showed higher performance at using GL with TiO_2/SiO_2 than that of using BL with TiO_2/SiO_2. For these reasons, GL was selected as a light source for setting of actual equipment. Furthermore, we have analyzed the wastewater using GC/MS. As shown Table 2, exsistance of organic compounds such as aniline and benzothiazole, which were not originally found in the flux of soldering, were found in before treatment wastewater. Toxic evaluation of wastewater after photodegradation is also required to measure the toxicity of reaction intermediates.

Table 2. GC/MS analysis result before and after treatment of wastewater.
(Software of Analysis: NAGINATA)

Before treatment		After treatment	
Chemicals	Concentration [μg/ml]	Chemicals	Concentration [μg/ml]
Pentacosane	1.34	Pentacosane	0.14
Aniline	2.91	N-nitrosomorpholine	0.49
Tricosane	0.97	Acetophenone	0.32
Heneicosane	0.95	Biphenyl	0.11
Timuvin 328	0.81	Benzothiazole	0.1
Heptadecane	0.82		
Benzothiazole	0.35		
Tetracosane	1.23		
Octadecane	1.14		
Eicosane	0.83		

References

[1]. K. Nakano et al. Separation and Purification Technology 34 (2004) 67-72.

PP-III-48

SBA-TYPE CATALYSTS IN DEGRADATION OF POLYPROPYLENE

Zeynep Obali, Naime Aslı Sezgi, Timur Doğu

Middle East Technical University, Chemical Engineering Department,
Ankara, Turkey, z_obali@yahoo.com

The dramatic growth of welfare levels in the second half of the 20th century has been accompanied by a drastic increase in plastic product use. This unavoidably has a huge impact on the environment, as it causes a rapid increase in the amount of plastic waste and hence a large strain on existing disposal methods such as landfill and incineration. Landfill space has been becoming scarce and expensive, a problem intensified by the fact that plastic waste is more voluminous than other waste types. Incineration, on the other side, could produce air pollution problems due to the possible toxic emissions. An alternative approach to the solution of problem caused by these wastes is the recycling of them by chemical recovery. In this method, the waste plastics are thermally non-catalytically or catalytically degraded into gases and oils. Major advantages of the catalytic thermal degradation over the non-catalytic process are lower operating temperatures and higher yields of valuable chemicals [1-3].

In this study, pure and Al-containing SBA-type catalysts were synthesized in order to be tested in the catalytic degradation of polypropylene. The pure SBA-type catalysts were synthesized using hydrothermal synthesis route and the aluminum containing ones were synthesized using impregnation method [4]. Tetraethyl orthosilicate was used as the Si source and aluminum isopropoxide and aluminum sulphate were used as the Al sources. It was observed that these materials had high surface areas in the range of 200-890 m^2/g and exhibited isotherms of Type IV. The aluminum incorporation into the structure was very effective. ^{27}Al MAS NMR spectra of the catalysts exhibited a mixture of tetrahedral and octahedral aluminum. TEM images showed well-ordered hexagonal arrays of uniform mesopores with channels. After the characterization of these catalysts, their performances have been investigated in polypropylene degradation reaction using a thermal analyzer. The TGA results showed a marked reduction in the degradation temperature and the activation energy in the presence of aluminum containing SBA-type catalyst, as shown in Figure 1. In the case of using aluminum isopropoxide as the aluminum source in the synthesis of the catalysts, the activation energy values were obtained in the range of 29-87 kJ/mol for catalysts having Al/Si ratios of 0.026-0.67 in the synthesized material, while the activation energy of polypropylene decomposition reaction in the absence of catalyst was about 172 kJ/mol. In the case of using aluminum sulphate as the aluminum source in the synthesis of the catalysts, the activation energy values of degradation reaction were found to be decreased down to about 49-73 kJ/mol.

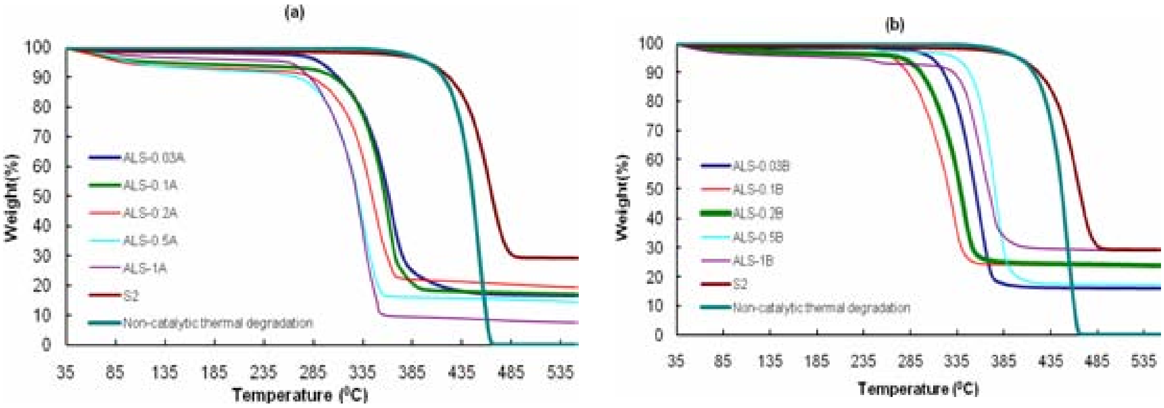


Figure 1. TGA plots describing the degradation of polypropylene over SBA-type catalysts synthesized using different aluminum sources: (a)$Al_2(SO_4)_3.18H_2O$, and (b)$C_9H_{21}AlO_3$.

References

[1]. Gobin, K., and G. Manos, Polym. Degrad. Stab., **2004**, 83, 267.

[2]. Lin,Y.-H. and H.Y. Yen, Polym. Degrad. Stab., **2005**, 89, 101.

[3]. Obalı, Z., Sezgi, N.A., and T. Doğu, Chem. Eng. Comm., **2009**, 196, 116.

[4]. Fulvio, P.F., Pikus, S., and Jaroniec, M., J. Coll. Inter. Sci., **2005**, 287 717.

Acknowledgements

Financial supports of Middle East Technical University through BAP-2007-03-04-08 and The Scientific and Technological Research Council of Turkey through 107M303 projects are gratefully acknowledged.

EXERGY ANALYSIS AND PROCESS INTEGRATION OF BIOETHANOL PRODUCTION FROM ACID PRE-TREATED BIOMASS: COMPARISON OF SHF, SSF AND SSCF PATHWAYS

Ojeda K.[a,b], Sánchez E.[a,b], El-Halwagi M.[b] and Kafarov V.[a]

[a]Research Center for the Sustainable Development in Industry and Energy, Department of Chemical Engineering, Industrial University of Santander
[b]Department of Chemical Engineering, Texas A&M University, United States of America. Fax: +57-7-6350540, Bucaramanga, Colombia. E-mail: cisyc@uis.edu.co

Abstract

Currently, there is a tremendous world-wide interest in the production of ethanol from biomass. One of the largest potential feedstock for ethanol is lignocellulosic biomass, principally agricultural residues. Cellulosic ethanol can be made from the stems, leaves, bagasse, stalks and trunks of plants which are not used for human-food production. However, there are significant economic challenges facing the second generation of biofuels. Consequently, application of process engineering is necessary to improve the overall process efficiency. Therefore, the main objective of this paper is to apply energy and exergetic analysis together with process integration methodologies coupled with process simulation as a unified and effective tool for the evaluation of converting lignocellulosic biomass to ethanol. In this paper, bioethanol production from acid-pretreated bagasse using different process configurations that include sequential hydrolysis and fermentation “SHF”, simultaneous saccharification and fermentation “SSF”, and simultaneous saccharification and cofermentation “SSCF”.

Introduction

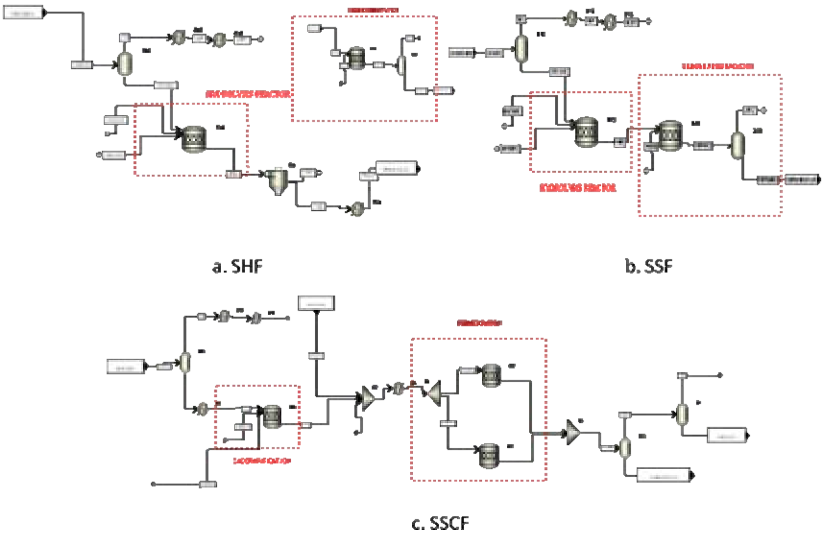
Conventionally, lignocellulosic biomass is pretreated by acid hydrolysis or chemical and physical methods, followed by enzymatic hydrolysis to open the plant fibers and to convert the polymers of cellulose and hemicellulose to sugars, which can be subsequently fermented[1]. The enzymatic hydrolysis of cellulosic materials by means of cellulase enzymes is one of the most promising advances in order to obtain products of great economic importance. This is a process catalyzed by a group of enzymes –cellulases- that are a mixture of different enzyme activities whose joint action produces the degradation of cellulose[1-3]. Research has been focused on improving various stages of production of bioethanol through enzymatic hydrolysis. Nonetheless, there is still much need for improving the process economics, and to determine the optimal type of enzymatic reactors to increase performance and energy efficiency, while reducing the costs and environmental impacts of the process[2].

Exergy analysis

Exergy analysis is a thermodynamic analysis technique based on the second law of thermodynamics which provides an alternative and illuminating means of assessing and comparing processes and systems rationally and meaningfully[3]. Exergy analysis yields efficiencies provide a true measure of how nearly actual performance approaches the ideal, and identifies more clearly than energy analysis the causes and locations of thermodynamic losses and the impacts on the natural environment. On the other hand, process integration is a holistic approach to process design and operation which emphasizes the unity of the process[4]. Both approaches provide useful tools for the synthesis, analysis, and optimization of processing pathways.

Cases study

Many flowsheet configurations have been proposed for ethanol production from lignocellulosic biomass, which incorporate pretreatment, hydrolysis and fermentation steps. In this study, bioethanol production from acid-pretreated bagasse using different process configurations (SHF, SSF, SSCF) was evaluated through exergy and process integration concepts. The configurations were simulated using Aspen^{TM} software (Fig. 1) in order to analyze the exergy and energy efficiencies of these systems and identify the targets for fresh and waterwaste through process integration to production of environmental friendly fuels.



a. SHF

b. SSF

c. SSCF

Fig. 1. Bioethanol process.

For the exergy analysis, the reference conditions were considered equal to the standard environmental conditions in Aspen^{TM} (T_0=298.15 K, p_0=101.3 KPa). Mole flows, molar fractions and molar enthalpy and entropy of material streams were taken from the Aspen^{TM} flowsheet results; each material stream was duplicated and brought to reference environmental conditions for the evaluation of the reference molar enthalpy and entropy. Exergy efficiencies of SHF, SSF and SSCF processes were 85%, 91% and 88% respectively.

The heat integration alternatives by pinch analysis were analyzed for SSF process. For this purpose, Aspen HX-NET® software was used. Balanced composite curve was generated and three pinch points were identified (174-169 °C), (168.3-163.3 °C), (35-30 °C). Using thermal pinch diagram and ΔT_{min}=5°C, the targets for minimum heating and cooling utilities requirements were calculated (0 and 7.431E+08 kJ/h, respectively). The SSF process can be improvement using the design of heat network for thermal integration of the process. The proposed HEN reduces cooling utilities by 10.7% and heating utilities by 97.5% (Table 1) and requires two new heat exchangers.

Table 1. Comparison – Network Performance

Requirements	Simulation Base	HEN
Heating Utilities[kJ/h]	5.643E+07	1.419E+06
Cooling Utilities[kJ/h]	8.335E+08	7.445E+08
Number of Units	17	19

References

[1]. Wall G. Exergy: a useful concept within resource accounting. Goteborg, Sweden: Institute of Theoretical Physics, Chalmers University of Technology and University of Goteborg; 1977.

[2]. Tomas-Pejo et al. Comparison of SHF and SSF processes from Steam-Exploded Wheat Straw for Ethanol Steam-Exploded Wheat Straw for Ethanol Steam-Exploded Wheat Straw for Ethanol cerevisiae Strains. Biotechnology and Bioengineering, 2008.

[3]. Wright, J. D. Evaluation of enzymatic hydrolysis processes, Energy from biomass and wastes, Ed. D. L. Klass, 1989.

[4]. El-Halwagi, M. M., “Process Integration”, Elsevier, 2006.

NEW CONCEPT FOR A SELF CLEANING HOUSEHOLD OVEN

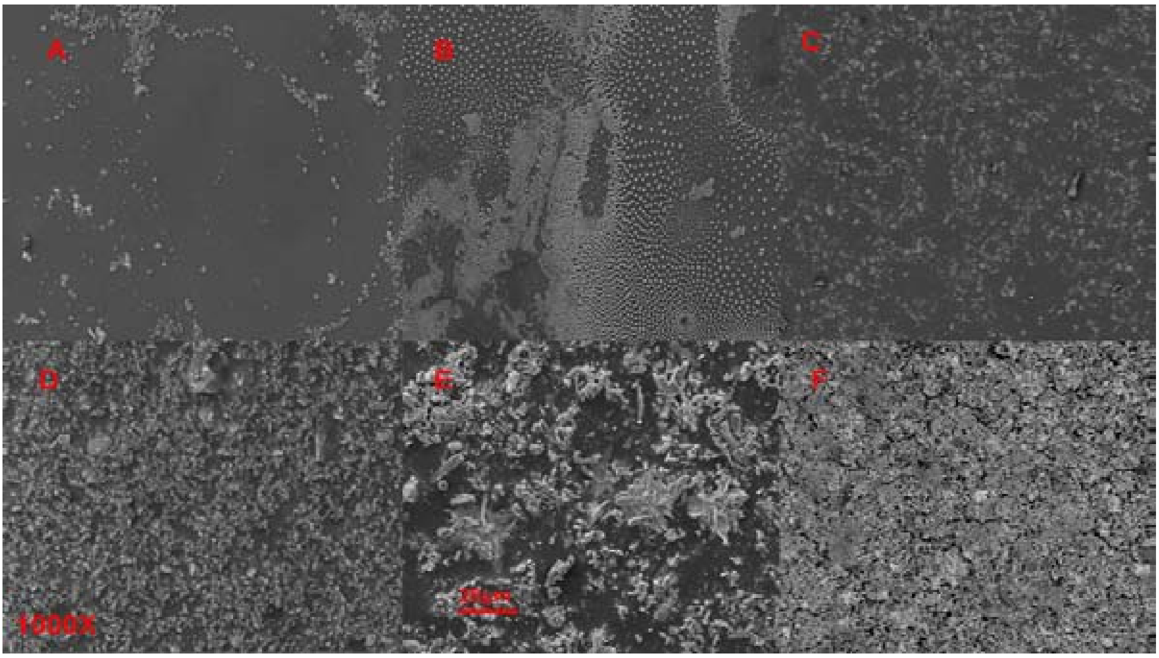
Pietro Palmisano, Hernandez S. P., Debora Fino, Nunzio Russo

Department of Materials Science and Chemical Engineering, Politecnico di Torino
Corso Duca degli Abruzzi 24, 10129 Torino, pietro.palmisano@polito.it

The household appliances industry has recently developed various solutions of self-cleaning oven [1,2] by means of a pyrolitic step at 550°C for 1h to reduce the residual soil, after a normal cooking cycle. The aim of this paper is to implement the concept of a self-cleaning household oven working at 400°C for 1h, by means of the catalytic activity of CeO_2 deposited over the oven walls as reported in our previous paper [3].

The first part of this work has been focused to assess the capability of the CeO_2 to promote the oxidation of selected cooking soils (milk in powder, tomato sauce, apricot jam, bouillon cube of fried ingrediants) by means of a TPC pilot described in [3]. The second step has been focused to compare various catalyst deposition methods over pieces (5X5cm) of oven walls based on a standard ceramic enamel. The gel-combustion, the sol-gel, the wet-urea and the powder coating deposition methods have been adopted. The obtained catalityc layers have been evaluated in terms of adhesion, penetration and exposed surface respect to the standard enamel layer used as support, using an SEM-EDS technique (Figure 1).

Samples prepared by means of the above mentioned deposition methods have been tested towards the abatement of cooking soils (listed above, plus olive oil) by means of gravimetric experiments carried out at 300°C and 400°C (for 1 hour) by measuring the weight before and after the thermal treatment which simulate a cooking cycle. The obtained results have been compared with those obtained by a pyrolitic enamel sample but at 550°C for 1 hour. Table I reports, for the sake of briefness, the percentages of residual olive oil resulting after the thermal treatment. The SEM micrographs reported in Figure1 show that the best CeO_2 layer has been obtained by means of the wet-urea deposition method. The gravimetric tests confirmed this consideration. The residual olive oil value, after 1h at 400°C, is comparable to the value measured at 550°C with the pyrolitic layer (1% and 0.5%, respectevely). It is worthwhile to notice that this new concept allows high energy saving and low insulating material costs.



,

Figure 1: A&B= commercial enamels (standard and pyrolitic), C,D,E,F=catalyzed enamels (powder coating, wet-urea, gel-combustion and sol-gel deposition methods).

Table I: gravimetric tests concerning the catalyzed and not catalyzed enamels using olive oil as soil

T [°C]	Coating	Residual Soil (olive oil)
300°C	Standard enamel (no cat.)	73.86
300°C	Pyrolytic enamel (no cat.)	59.64
300°C	powder coating	56.6
300°C	sol gel	47.03
300°C	gel combustion	31.14
300°C	wet-urea method	19.49
400°C	Standard enamel (no cat.)	39.28
400°C	Pyrolytic enamel (no cat.)	33.28
400°C	powder coating	21.04
400°C	sol gel	14.1
400°C	gel combustion	18.43
400°C	Wet-urea method	1.04
550°C	Pyrolytic (no cat.)	0.51

References

[1]. E. Scholtes, Patent GB1457579, “Pyrolytic Self Cleaning Cooker Ovens” **(1978).**
[2]. GfK Marketing Services Italia – Global Appliances Market Survey **(2006)**.
[3]. P. Palmisano, P. Faraldi, D. Fino, N. Russo, *Topics in Catalysis* **(2009)** 154, 254-257.

Acknowledgement

The authors would like to thank Indesit Company S.p.A. for the financial support.

HYDROGEN PRODUCTION BY METHANOL STEAM REFORMING OVER COBALT CATALYSTS

Papavasiliou J.[1], Papadopoulou E.[1,2], Ioannides T.[1]

[1]Foundation for Research and Technology-Hellas (FORTH), Institute of Chemical Engineering and High Temperature Chemical Processes (ICE-HT), Patras, Greece
[2]Department of Chemical Engineering, University of Patras, Patras, Greece

Introduction

The primary fuel for PEM fuel cells is H_2, which can be supplied from liquid fuels, such as methanol, ethanol, and others. Steam reforming of methanol (SRM) can provide a product gas with high H_2 content (up to 75%) and low CO concentration (1-2%). The high oxygen mobility and strong interaction with other phases make CeO_2 a very interesting support or promoter for catalysts used in reactions involving hydrogen. Moreover, many authors have highlighted zirconia as a suitable support due to its high thermal and mechanical stability and redox properties. The insertion of ZrO_2 into the CeO_2 structure has been reported to enhance its redox properties as well as the thermal stability [1]. Consequently, CeO_2-ZrO_2 has shown a great potential as a catalyst support of reforming catalysts. Cobalt-based catalysts have been reported to have superior ethanol steam reforming performance due to their high activity in C–C bond cleavage at temperatures as low as 350–400 °C [2]. In spite of dissimilarities reflecting differences in molecular structure, there are several marked common features of methanol and ethanol in reforming processes. In this preliminary work, cobalt-based catalysts, i.e. Co-Ce, Co-Zr and Co-Ce-Zr mixed oxides, were prepared by two different methods, urea-nitrate combustion method (CM) and molten salts method (MSM), and tested on SRM.

Experimental

Co/CeO_2, Co/ZrO_2 and Co/CeO_2-ZrO_2 (16 wt% CeO_2/ZrO_2) catalysts were prepared by two different methods, CM [3] and MSM [4]. All catalysts contained 10 wt% Co. The effect of preparation parameters (i.e. urea content in the CM and water addition in the MSM) on the catalytic properties of Co based catalysts were also investigated.

XRD patterns of the oxides were collected with a Bruker D8 Advance diffractometer using Cu K_a radiation. The specific surface area (S_{BET}) of the samples was analyzed by N_2 adsorption using a Quantachrome Autosorb-1 instrument.

The SRM reaction was carried out in a conventional flow reactor at atmospheric pressure. All runs were performed using 0.1 g of catalyst diluted with 0.9 g sand, with no reduction pretreatment, under a reactant flow rate of 100 cm^3 min^{-1}. The composition of the reaction gas was 5% MeOH, 7.5% H_2O in He. Gases in the effluent were analyzed by a Shimadzu GC-2014 equipped with TCD and FID.

Results and discussion

The surface area of all combustion-prepared catalysts was smaller than 9 m^2 g^{-1}. XRD analysis of fresh catalysts revealed that most of the diffraction peaks correspond to support phases (ZrO_2 or CeO_2), while peaks of the Co_3O_4 phase were also present. XRD peaks due to CeO_2 oxide were not detected, most probably due to incorporation of ceria in the zirconia lattice. On the other hand, cobalt catalysts prepared by MSM had much higher surface area (Co/CeO_2-ZrO_2: 140 m^2/g), but CeO_2 was detected as a separate phase in the Co/CeO_2-ZrO_2 sample.

From the combustion synthesized samples, Co/CeO_2-ZrO_2 prepared with 200% urea excess had the best catalytic behaviour (100% MeOH conversion at 425 °C), while all the samples were more selective towards CO production than CO_2. Molten salt method resulted in more active (100% MeOH conversion at 400 °C) catalysts. The reaction pathway appears to consist of methanol decomposition followed by the water-gas shift reaction.

Conclusions

In this study Co-Ce-Zr catalysts were prepared via a) the combustion and b) the molten salts method and tested for the SRM reaction. The resulting material characteristics were influenced by the urea/nitrate molar ratio used in the combustion synthesis and the water addition during the molten salts method. The latter method resulted in more active SRM catalysts.

References

[1]. S.S.-Y. Lin, S.Y. Ha, D.H. Kim, Catal. Lett. 122 (2008) 295-301.
[2]. H. Song, U.S. Ozkan, J. Catal. 261 (2009) 66–74.
[3]. J. Papavasiliou, G. Avgouropoulos, T. Ioannides, Catal. Commun. 6 (2005) 497-501.
[4]. P. Afanasiev, C. Geantet, Coordin. Chem. Rev. 178–180 (1998) 1725–1752.

CATALYTIC UPGRADING OF PRODUCT GAS FROM GASIFICATION OF COFFEE BEAN WASTE BY OLIVINE AND Ni/OLIVINE

Chiravoot Pechyen[1], Duangduen Atong[2], Duangdao Aht-Ong[3,4], and Viboon Sricharoenchaikul[5]

[1]Department of Packaging and Materials Technology, Faculty of Agro-Industry, Kasetsart University, Bangkok, 10900, Thailand
[2]National Metal and Materials Technology Center, Thailand Science Park, Pathumthani, 12120, Thailand
[3]Department of Materials Science, Faculty of Science, Chulalongkorn University,
[4]Research Unit of Advanced Ceramics and Polymeric Materials, National Center of Excellence for Petroleum, Petrochemicals and Advanced Materials, Chulalongkorn University, Bangkok, 10330, Thailand
[5]Department of Environmental Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok, 10330, Thailand, viboon.sr@chula.ac.th

Hydrogen is regarded as the energy for future with its cleanness and high calorific value and has become a focus of renewed interest in many parts of the world. In present, most of hydrogen is generated in large scale from fossil fuel via steam reforming and gasification. These production pathways are not environmentally sound and economically viable solution and result in significant CO_2 emissions. Biomass energy has significant environmental benefits including lower emissions of CO_2 and other greenhouse gases. However, one of the major issues in biomass gasification is tar formation. Tars are complex mixture of condensable hydrocarbons which include single ring to five ring aromatic compounds along with other oxygen containing hydrocarbons. Tars may be eliminated by the use of catalytic cracking process. In this work, olivine based catalysts were prepared and tested for reforming of tar from gasification of coffee bean waste. The waste was collected from the Mae Fah Luang Foundation under Royal Patronage (Doi Tung), Chiang Rai province, Thailand. Their particle sizes were between 0.4 to 0.5 mm with proximate and ultimate analyses shown in Table 1.

Table 1. Chemical characteristics of Coffee bean waste raw materials

Proximate analysis (wt%)		Ultimate analysis[a] (wt%)		Chemical composition (wt%)	
Volatile	80.04	Carbon	50.80	Cellulose	40.64
Fixed carbon	14.23	Hydrogen	6.40	Hemicellulose	25.91
Ash	3.56	Nitrogen	3.10	Lignin	31.82
Moisture	2.17	Oxygen[b]	39.70		

[a] Moisture and ash free. [b] By difference.

Olivine may be an interesting support for nickel, giving a system with high attrition resistance and strong linking with nickel. The nickel/olivine catalyst was synthesized via impregnation method. The TGA/DTA results of the $LiFePO_4$ precursor performed under flowing nitrogen was shown in Figure 1. While the broaden endothermic peaks attributed to water evaporation was found at temperatures between 60°C and 160°C, the small endothermic peaks at 250°C caused by organic compound decomposition were also observed. The peak appeared at 500°C is due to the crystallization of $LiFePO_4$. This result corresponded well with the continuous weight loss from ambient temperature to ~550°C. The observed initial weight loss before 160°C, the step weight loss between 170°C and 270°C, and the final weight loss from 450-550°C corresponded to the elimination of absorbed water, decomposition of organic compounds, and crystallization of phosphate, respectively. Therefore the precursor was calcined above 550°C to obtained $LiFePO_4$ crystallized phase. This agreed well with the results from the XRD analysis.

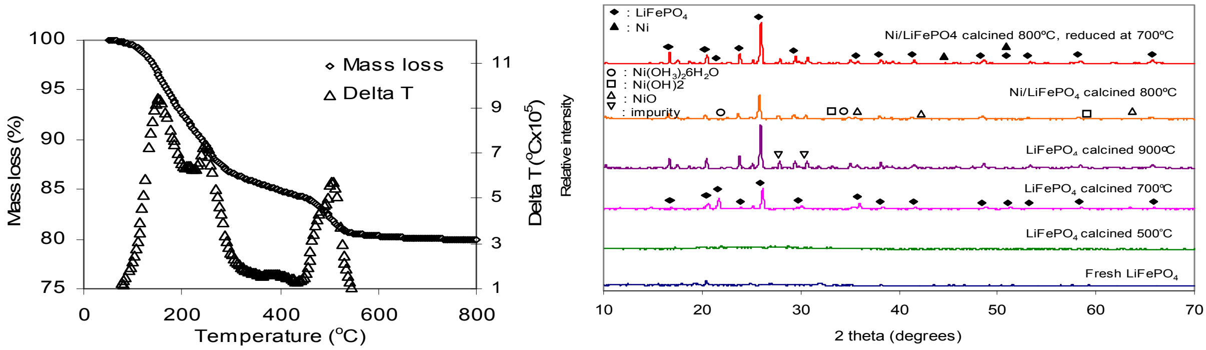


Figure 1. The TGA/DTG curves for the $LiFePO_4$ olivine (left) and XRD patterns of olivine and Ni/olivine prepared at stated conditions (right).

XRD of the Ni/ $LiFePO_4$ catalyst calcined at 800°C, with a support calcined at 700°C, shows that the olivine phase is maintained along with trace amount of phases related to Ni (Ni, NiO, $Ni(OH)_2$, $Ni(NO_3)_26H_2O$). After reduction process at 700°C, signals of NiO and other intermediate phases related to Ni became less pronounced while intensity lines of Ni phase were amplified. Prepared catalyst was tested by placing in a secondary reactor receiving producer gas from a laboratory scale primary continuous fixed bed gasifier firing coffe bean waste at 1.5 g/min. Product gases were simultaneously measured using dedicated TCD-NDIR analyzer. In general, addition of olivine or Ni/olivine significantly improves both quality and quality of product gases as noticed from superior gas yield, LHV, H_2/CO ratio, as well as cold gas efficiency with highest enhancement attained with nickel catalyst. In real practice, using only olivine may be sufficient due to high cost of nickel and its vulnerability to various metal poisoning substances.

CATALYTIC CONVERSION OF FISCHER-TROPSCH WAX ON Pt/AlSBA-15 AND Pt/β ZEOLITE CATALYSTS

György Pölczmann[1], József Valyon[2], Jenő Hancsók[1]

[1] *University of Pannonia, Department of Hydrocarbon and Coal Processing,*
e-mail: hancsokj@almos.uni-pannon.hu
[2] *Chemical Research Center, Institute of Chemistry, Hungarian Academy of Sciences*

Because of the more serious problems with the environment and the crude oil supply the use of fuels and lubricants produced from renewable feedstocks has come to the front nowadays. Accordingly it is very important to develop a catalytic system (identification of the proper catalysts and advantageous process parameters) that can be applied to produce the target product (mixture of gas oil and base oil) with selective isomerization (skeletal arrangement) and with high isoparaffin selectivity from solid n-paraffin mixtures produced with Fischer-Tropsch synthesis [1-3]. The isomerization of high molecular weight n-paraffins can be effectively carried out on bifunctional catalysts. There are only a few indications about the application of metal catalysts on mesoporous carrier in the literature. [4,5]. Consequently our objective was to investigate a Pt/AlSBA-15 catalyst which has not been investigated in detail in this reaction system yet, compared with a Pt/beta zeolite which was earlier applied for isomerization of high molecular weight n-paraffins [4,6].

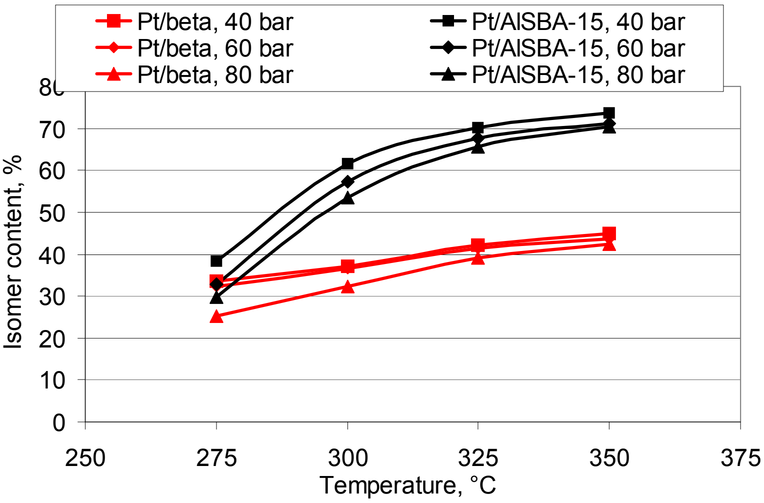


Figure 1: The effect of process parameters to the isomer contents of the liquid products (LHSV = 1 h^{-1}).

The applicability and catalytic activity of Pt/AlSBA-15 and Pt/beta zeolite catalysts of 0.45 % platinum content for the selective isomerization of Fischer-Tropsch wax was investigated in the present experiment. The experiments were carried out in a high-pressure microreactor system in continuous operation and on a catalyst with steady-state activity. The main properties of the feedstock which was a mixture of paraffin produced by Fischer-Tropsch synthesis (the synthesis gas was produced from biomass) were: n-paraffin content (C_{18}-C_{57}): 97.4%, sulphur content: < 5 mg/kg, pour point: 72 °C. In the experiment the following process parameters were applied: T= 275-375 °C, P=40-100 bar, LHSV=1.0-3.0 h^{-1}, H_2/hydrocarbon ratio: 400-800 Nm^3/m^3. The composition of the products was determined by gas chromatography.

From the catalysts with different carriers the best results were gained on the Pt/AlSBA-15 catalyst. On this catalyst and with increasing temperature the yield of liquid products (C_{5+}) decreased, but until 325 °C this value was above 95% in every case. But on the Pt/beta catalyst the amount of gas products increased significantly over 300 °C. In case of of both catalysts in the gas products mainly branched isobutane was identified, which indicated that the cracking enacted partly after the isomerization reactions. The isoparaffin contents of the liquid products (Figure 1) in the function of process parameters increased with increasing temperature and decreased with increasing pressure and LHSV in every case while other parameters were kept constant, but - as we mentioned earlier -. On the Pt/beta the yield of liquid products was not sufficient. Based on the isoparaffin contents of the different fractions produced on Pt/AlSBA-15 it can be concluded that at advantageous process parameter combinations (T=300-325 °C, P=40-70 bar, LHSV=1.0-2.0 h^{-1} / T=275-300 °C, P=40-70 bar, LHSV=1.0-2.0 h^{-1}) the catalyst was applicable to produce C_{11}-C_{20} and C_{21}-C_{30} fractions with high isoparaffin content (63.5-85.6% / 34.1-58.7%) with adequate yields (29.9-36.6% / 46.2-58.8%).

To summarize it, it was concluded that the catalysts with AlSBA-15 carrier showed the better results in the production of gas oil and base oil fractions with high isoparaffin content from Fischer-Tropsch wax, because of its higher isomerization and milder cracking activity. The selectivity of the target product fractions was high, and based on these facts the selective isomerization of the Fischer-Tropsch wax is a new application area of the Pt/AlSBA-15 catalyst.

References

[1]. Zhou, Z., Zhang, Y., Tierney, J.W.: „Producing fuels from Fischer-Tropsch waxes", PTQ, **2004**, 4, 137-143.

[2]. Vosloo, A.C.: „Fischer-Tropsch: A futuristic view", Fuel Processing Technology, **2001**, 71, 149-155.

[3]. C. Bouchy, G. Hastoy, E. Guillon, J.A. Martens: „Fischer-Tropsch Waxes Upgrading via Hydrocracking and Selective Hydroisomerization", Oil & Gas Science and Technology, **2009**, 64, 91-112.

[4]. Deldari, H.: „Suitable catalysts for hydroisomerization of long-chain normal paraffins", Appl. Catal. A: General, **2005**, 293, 1-10.

[5]. Rosetti, I., Gambaro, C., Calemma, V.: „Hydrocracking of long chain linear paraffins", Chemical Engineering Journal, **2009**, 154, 295-301.

[6]. Soualah, A., Lemberton, J.L., Pinard, L., Chater, M., Magnoux, P., Moljord, K.: "Hydroisomerization of long-chain n-alkanes on bifunctional Pt/zeolite catalysts: Effect of the zeolite structure on the product selectivity and on the reaction mechanism", Appl. Catal. A: General, **2008**, 336, 23-28.

PROCESS FOR THE PRODUCTION OF BUTYL LACTATE

**Prokhorov Alexiy[1], Shvets Valeriy[1], Suchkov Yuriy[1], Kozlovskiy Ivan[1],
Kozlovskiy Roman[1], Makarov Mikhail[1], Kapustin Alexey[2]**

[1]D. Mendeleev University, Miusskaya sq., 9, Moskow, Russia, proxorov.al@mail.ru
[2]Azov State University, Mariupol, 87500, Ukraine

Butyl lactate (BL) is high-boiling, nontoxic and biodegradable substance and because of its properties BL is widely used as a solvent for nitrocellulose, oils, dyes, natural gums, many synthetic polymers etc., supplanting traditional toxic solvents and reagents (aromatic and chloroorganic compounds). Besides BL is a key intermediate for production of many chemicals such as, lactide, propylene glycol, herbicide, medicine, food or cosmetic additive, etc.

The periodical method of processing of a solution of ammonium lactate produced by fermentation to lactic acid esters by reaction of an aqueous ammonium L-lactate solution (68%) with alcohol is known. Preferably, the reaction is carried out in the bath reactor under reflux. The eliminated ammonia and water together with alcohol (azeotropic mixture) remove from system. Reaction time for noncatalytic reaction is from 10 to 17 hours.

In present work the influence of different catalysts on the rate of esterification of ammonium lactate with butanol was investigated. Estimation of efficiency of catalysts was carried out by comparison of rates of elimination of water.

Also, influence of different methods of cleaning of solutions of ammonium lactate (by using of different absorbents, coagulants and others substances), produced by fermentation, on the yield of ester has been examined.

Carrying out of reaction of ammonium lactate with butanol in the presence of the catalysts allows to reduce process duration by 25-30%.

The use of adsorbents on the clearing stage (various types of bentonites and the active carbon) allows to increase the yield of ester from 60 % to 75 %.

PP-III-55

EXPERIMENTAL ANALYSIS OF SOOT ABATEMENT IN REDUCING SYNGAS FOR HIGH TEMPERATURE FUEL CELL FEED

Raimondi A.[1], **Loukou A.**[2], **Fino D.**[1], **Saracco G.**[1], **Trimis D.**[2]

[1]*Department of Materials Science and Chemical Engineering, Politecnico di Torino, Turin, Italy, corresponding author: andrea.raimondi@polito.it*
[2]*Insitute of Thermal Engineering, TU Bergakademie Freiberg, Freiberg, Germany*

A novel approach for removing soot emitted by a Thermal Partial Oxidation (TPOX) reactor was investigated experimentally. According to this new route soot gets retained within a SiC wall-flow filter and reacted away by the synthesis gas (syngas) flow at high-enough temperatures and suitable operating conditions. This technique was developed to satisfy the stringent specifications of a small-scale combined-heat-and-power (CHP) unit for domestic appliances based on SOFC fuel cells.

The possibility to remove soot in a very reducing atmosphere, with no oxygen addition, has indeed been previously presented by the same authors [1,2,3], in order to develop a simple and low-cost solution to protect the anode of a SOFC (Solid Oxide Fuel Cell), fed by the syngas produced by an innovative hydrocarbon multi-fuel processing unit based on porous ceramic media [3,4]. The previous results showed the possibility to achieve an equilibrium between the soot retained within the trap channels and the soot that is removed by gasification, simply setting the air to fuel ratio of the TPOX syngas generator at low enough values. The proof of concept has been presented. Despite this solution can represent an interesting option for systems based on fuel cell applications, the kinetics involved appeared rather slow compared to direct combustion of soot in alternative appliances (e.g. soot trap regeneration in car exhaust treatment). The present investigation aims at exploring pathways to accelerate the soot conversion process, by investigating the effect on soot abatement of different input parameters such as the lambda factor, the specific power density and the air pre-heating. The best operating conditions are tentatively pointed out for the novel soot abatement system proposed. The dynamics of soot deposition/ gasification within the filter has been monitored as pressure drop between inlet and outlet of the trap.

The tests have been carried out by loading the soot trap until a value of 6 mbar at 8 kW of thermal load and at a lambda value of 0.40. The loading conditions have been previously fixed and maintained for all the tests, in order to achieve a fast loading of the soot trap and guarantee the same initial conditions to all experiments. Hence, the system has been shifted to defined conditions and the regeneration effect monitored.

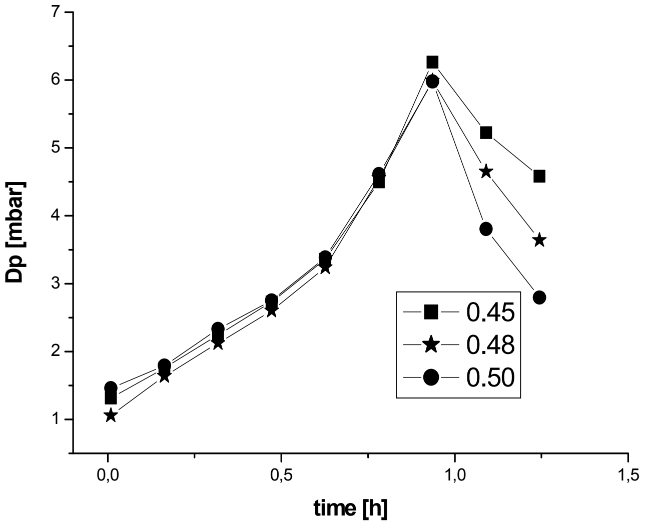


Fig.1: effect of lambda on the regeneration of the soot trap performing the system at 8 kW of thermal load.

A number of results as those depicted in Fig. 1 (effect of lambda on regeneration speed) have been gathered. These results indicate feasibility of an easy and practical solution for small-scale CHP applications based on fuel cells, requiring effective removal of soot with no use of oxygen for safety and anode stability reasons.

References

[1]. A. Raimondi, D. Fino, G. Saracco, New concept for soot removal from a syngas mixture, J. Power Sources, **(2009)**, Vol.193, 338-341.

[2]. A. Raimondi, A. Loukou, S. Voss, D. Fino, D. Trimis, Innovative regeneration strategy for a soot trap coupled to a TPOX reactor, 32nd Italian Meeting on Combustion, **(26-28 april 2009)**, Naples (Italy).

[3]. A. Loukou, A. Raimondi, D. Trimis, G. Saracco, An innovative hydrocarbon fuel processing unit on the basis of combined operation of a thermal partial oxidation reformer and a self-regenerable soot particle filter, 10th Conference on Energy for a Clean Environment, **(7-10 July 2009)**, Lisbon (Portugal).

[4]. A. Loukou, S. Voss, M. Mendes, A. Raimondi, D. Trimis, Parametric experimental investigation of a small scale packed bed reactor for Thermal Partial Oxidation, 4th European Combustion Meeting, **(14-17 April 2009)**, Vienna (Austria).

Acknowledgements

The authors would like to thank the European Commission for the financial support of this work within the 6th framework program, project FlameSOFC, contract no.019875 (SES6).

PP-III-56

THE METHOD FOR PRODUCING OF MOTOR FUEL COMPONENTS FROM NATURAL CARBOXYLIC ACIDS

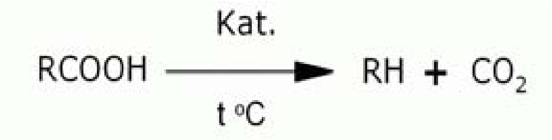
Romanova Anastasiya, Shvets Valeriy, Suchkov Yury, Korneev Igor

D. Mendeleyev University of Chemical Technology of Russia, Moscow, Russia
liceistka2003@mail.ru, hxc@muctr.ru, +7(499) 9789554

The world's fossil fuel resources – including crude oil, natural gas and coal – are huge, however they will be exhausted sooner or later. There is already fossil fuel deficit leading to a rise of motor fuel prices. As a result use of renewable energy sources expands steadily. Thus, the most significance acquires a biofuel produced from vegetable oils, animal fats, or its derivatives, particularly, fatty acids.

In literature there are a lot of works devoted to the process of producing the biofuel engine. At present biodiesel is extensively produced both in the USA and Europe. This fuel consists of methyl esters of the fatty acids (FAME) of the parent oil and fat. Biodiesel is better than petrodiesel in terms of sulphur content, flash point, aromatic content and biodegradability. But biodiesel is a better solvent than petrodiesel, and has been known to break down deposits of residue in the fuel lines of vehicles that have previously been run on petrodiesel. Another disadvantage of biodiesel is that it has lower energy content, since diesel engines inject equal volumes of fuel so power drops 8%. These disadvantages can be avoided if not FAME but hydrocarbons are produced from triglycerides of oil or from pure fatty acids.

In the current report we present results of investigation of process for production of biofuel by decarboxylation of fatty acids, which in perspective should be a key stage in obtaining hydrocarbons containing 15-21 carbon atoms. This type of fuel can be termed as biofuel II generation.



$$RCOOH \xrightarrow[t\,^{\circ}C]{Kat.} RH + CO_2$$

The influence of reaction conditions (such as temperature, pressure, catalyst type and feed rate of stock) on conversion and selectivity of process decarboxylation of fatty acids was investigated and optimal ranges of these parameters were determined.

As a catalyst the series of compounds from a number of industrial catalysts of hydrorefining, individual and supported zeolites and many others, were tested. It was found that the most efficient catalysts are γ-alumina and supported zeolites. Also it was found that this catalysts are deactivated in time. However after decrease their activity (after deactivation, activity loss) the given catalysts can be exposed to regeneration and reused repeatedly.

PP-III-57

CHEMICAL COMPOSITION OF CATALYSTS AND KINETICS OF HIGHER PARAFFINS DEHYDROGENATION

Romanovskiy R.V., Youriev E.M., Frantsina E.V., Dolganov I.M., Kravtsov A.V.

Tomsk Polytechnic University, Lenin Street, 30, 634050, Tomsk, Russia;
Fax: +7(3822)563-435; ravix@sibmail.com

Higher paraffins (C_{10}-C_{13}) are dehydrogenated to produce linear alkylbenzene (LAB) – the most common raw material in the manufacture of biodegradable household detergents. This is a production of high priority so raising its efficiency is very important. Selectivity of the process depends on the catalyst used in the first place. Therefore, testing and selection of most efficient catalyst defines performance of the entire installation.

This work is devoted to researching changes in characteristics of catalysts depending on promoters' contents like Sn, alkali and earth metals. Quality and quantity of promoters have significant impact on catalyst operation [1-3]. Samples of three types of catalysts marked as CD-1, CD-2 and CD-3 were analyzed by SEM method using equipment of TPU Nano-Centre – JSM-7500FA microscope. Analysis proved that all samples were Pt catalysts on γ–Al_2O_3 with promoters. Mass concentration for Al and O was roughly the same for all samples and much greater than promoter concentration. However, Pt (main dehydrogenation component) content decreases from first to last sample while production experiments in Pacol™ process showed that activity, selectivity and operation life of these catalysts are actually increasing [4]. Therefore, quality of catalysts work is defined equably by content of main component (Pt) and additional components.

Characteristic	CD-1	CD-2	CD-3
Na content, mass %	0,06	—	0,88
K content, mass %	0,18	—	0,21
Cu content, mass %	0,32	0,16	0,06
Sn content, mass %	0,64	0,40	0,50
Pt content, mass %	0,94	0,84	0,85
Operation life (approx.), days	180	200	250

Thus, there is a significant increase in sodium content among the samples. The first sample contains almost no sodium, but a small content of potassium; the second sample does not contain sodium and potassium; the third sample contains considerable amount of sodium and a small content of potassium. Alkali metals apparently serve as acid sites blockers and hydrogen activators and also decrease the speed of coke formation.

There is a significant decrease in Cu content along with an increase in catalytic characteristics. Copper intensifies side reactions that lead to coke formation and degradation of product quality.

Besides stated above, there are changes in contents of some other elements through the samples. In whole, analysis results prove correspondence between industrial experiment and computing experiment. The computer modeling system based on physicochemical foundations of the process [5] adequately describes the process for obtaining LAB. This system considers differences between catalyst types by using specific kinetic parameters for each type. The results of quantitative analysis of catalyst samples should correlate to corresponding catalytic properties – activity, selectivity and deactivation rates. On the other hand, they do – similar changes of properties are observed in the computer model. Dynamics of corresponding coefficients and constants used for computing operation of specific type of catalyst correlate to dynamics of content changes of respective promoters.

References

[1]. S. He, C. Sun, Z. Bai, X. Dai, B. Wang Dehydrogenation of long chain paraffins over supported Pt-Sn-K/Al2O3 catalysts: A study of the alumina support effect // APPL CATAL A-GEN. – 2009 (356), p. 88-98.

[2]. G. Zahedi, H. Yaqubi, M. Ba-Shammakh Dynamic modeling and simulation of heavy paraffin dehydrogenation reactor for selective olefin production in linear alkyl benzene production plant // APPL CATAL A-GEN. – 2009 (358), p. 1-6.

[3]. D.T. Gokak, A.G. Basrur, D. Rajeswar, G.S. Rao and K.R. Krishnamurthy Lithium promoted Pt-Sn/Al2O3 catalysts for dehydrogenation of n-decane: influence of lithium metal precursors.

[4]. A.V. Kravtsov, E.N. Ivashkina, E.M. Youriev, E.D. Ivanchina IT-technologies in the decision of problems of industrial dehydrogenation process of n-paraffin – Tomsk: STT, 2008. – 230 p.

[5]. Kravtsov A.V., Ivanchina E.D., Ivashkina E.N., Youriev E.M. Improving the process of higher paraffindehydrogenation on the basis of nonstationary kinetic model // XVIII International Conference on Chemical Reactors CHEMREACTOR-18. Abstracts. – 2008, p. 325-326.

PP-III-58

COMPARISON OF Ti/SnO_2-Sb_2O_5 AND Ti/Pt-Ru ANODES FOR OXIDATION OF WATER CONDENSATE RECOVERED IN A SHUTTLE ORBITER

Rutigliano L., **Fino D.**, **Specchia V.**, **Spinelli P.**

Department of Materials Science and Chemical Engineering,
Politecnico di Torino,
Corso Duca degli Abruzzi 24, 10129, Torino, Italy
Tel./Fax 011.564.4710/4699; corresponding author: debora.fino@polito.it

Regenerative processes are required to recycle the cabin air during manned missions in space and, in particular, to recover wastewater. Water is produced aboard the shuttle orbiter from different sources: hygiene water, urine, and humidity condensates.

Electrooxidation of humidity condensates recovered aboard of shuttle orbiters (initial TOC = 95 ppm), was carried out with a particular electrochemical cell, where the anodes used for oxidation of the organic pollutants require high oxygen over-potential to produce high concentration of the hydroxyl radical, which is the strongest oxidant agent generated by an electrochemical process [1].

The deposition of SnO_2/Sb_2O_5 on the pure titanium foils used as support was realized with several techniques using as precursor $SnCl_4$ and $SbCl_3$ into 2-propanol; Ti/Pt-Ru was, instead, a commercial electrode [2]. The Ti/SnO_2-Sb_2O_5 was fully characterized by XRD, SEM, EDS, etc. Some of the main contaminants, for example phenol, dissolved in the humidity condensate were chosen and dissolved in an aqueous feeding solution to carry out the cyclic voltammetry (CV) analyses.

Tests for the abatement of these organic compounds, considered globally ac TOC, were performed under galvanostatic condition (0.4 – 18 mA/cm^2), by monitoring during time chemical species dissolved using spectrophotometer, HPLC analysis [3].

FESEM-EDS and ATR-FTIR allowed to detect organic molecules present on the electrode surface in both the adsorbed or polymerized form. A further confirm was given by cyclic voltammetries, which showed clearly the formation of a slightly passivating polymeric film on the electrode surface.

The main limit electro-oxidation is related to the deposition of the dissolved contaminants on the electrode surface and the formed film layer avoids any further oxidation; therefore, particular attention was given to reactivate the anodes.

The re-activation of the electrode surface was possible with potentiostatic tests by anodically polarizing the electrode above 1.1 V (vs Hg/Hg_2SO_4). The electro-oxidation tests were carried out in galvanostatic conditions with a current density between 0.4÷18 mA cm^{-2} to understand the influence of the anodic current on the organic decomposition rates and with different ion exchange membranes.

Several regenerative treatment runs were performed with the solution simulating the shuttle condensate water to determine the evolution, during the tests, of the total organic carbon (TOC) concentration, the oxidation intermediate products, the nitrogen molecular concentration using a colorimeter (Orbeco-Hellige model 975-MP) or a spectrophotometer (DR 5000 Hach-Lange), furthermore the pH and conductivity were monitored during the tests. Fig. 1 compares the TOC abatement for the two different anodes at a current intensity of 0.2 A; a remarkably better performance of the SnO_2-Sb_2O_5 electrode over the commercial one can be observed.

Furthermore, the inversion of the electrode polarity, indicated by small arrows in Fig. 1, seemed to offer a further advantage

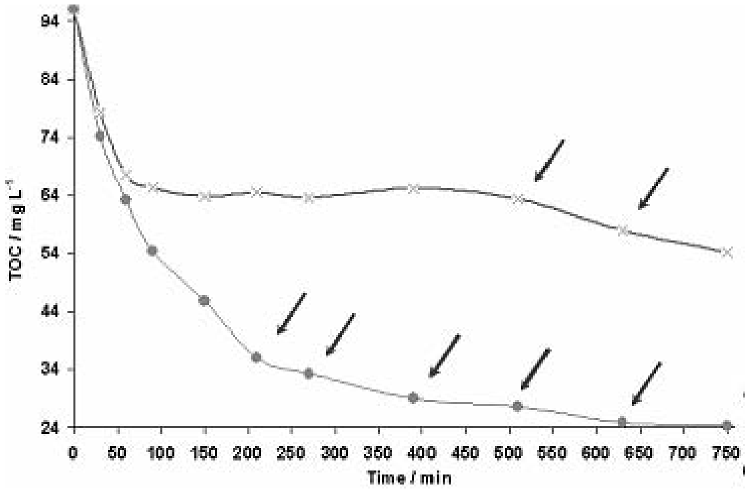


Figure 1. Comparison of the TOC evolution vs time between the Pt/Ru and SnO_2/Sb_2O_5 anodes in humidity condensates electro-oxidation test in divided cell at 0.2A; Pt/Ru CM (×); SnO_2/Sb_2O_5 CM (●). Electrolyte: Na_2SO_4 0.01 M

Test carried out in presence of free chlorine seems to improve the TOC abatement efficiency forming hypochlorous acid.

References

[1]. Comminelis C., De Battisti A., J. Chim. Phys. **(1996)** 93, 673-679.

[2]. Yao P., Chen X., Wu H., and Wang D., Surf. Coat. Tech **(2008)** 202, 3850-3855.

[3]. Rutigliano L., Fino D., Saracco G., Specchia V., Spinelli P., and Grizzaffi L., J. Appl. Electrochem. **(2009)** 39, 2239-2249.

PP-III-59

PHYSICOCHEMICAL PROPERTIES OF THE SOLUTIONS OF BIOREGULATORS FOR BIOCHEMICAL PURIFICATION OF WASTEWATER

**Ryzhkina I.S.[1], Murtazina L.I.[1], Kiseleva Yu.V.[1], Konovalov A.I.[1],
Pantukova M.E.[2], Pavlova T.P.[2], Fridland S.V.[2]**

*[1]A.E. Arbuzov Institute of Organic and Physical Chemistry KazRC RAS,
8 ul. Akad. Arbuzova 420088 Kazan. E-mail: ryzhkina@iopc.kcn.ru
[2]Kazan State Technological University, Engineering Institute of Chemical Technology, Kazan*

To improve the process of biochemical treatment of highly toxic wastewater are applied bioregulators activity of microorganisms. Now we are carried out search of new synthetic bioregulators capable at low (including 10^{-12} mol/L) and ultralow (10^{-15} mol/L and below) concentrations to increase the rate of wastewater treatment. This approach can considerably reduce the consumption of a bioregulator and exclude practically its influence on the purified water. However, the application of biologically active substances at low and ultralow concentrations in wastewater treatment technology is connected with a number of difficulties. One of the more important aspects of the problem is the absence of the knowledge that can explain and predict the occurrence of nonlinear concentration dependences of the physicochemical properties and bioeffects of solutions, change “a sign” of bioeffects at the transition from one concentration range to another. For example, the addition of synthesized by us bioregulator of activity of microorganisms salt of N,N-diphenylguanidin and dihydroxymethylphosphinic acid (**1**) decrease the rate of purification process of wastewater at a concentration 10^{-5} mol/L, and increases it at a concentration 10^{-11} mol/L. The practical use of such phenomena is constrained by the lack of an explanation of their physicochemical essence. Recently, we showed experimentally for the first time, that in aqueous solutions of certain biologically active substances, in low and ultralow concentration range nanoassociates with size of about 200 nm are formed. The concentration dependences of the physicochemical properties and nanoassociates sizes, and electrokinetic potential (zeta-potential) are related to nonlinear concentration-bioeffect dependences [1, 2]. In this work we discuss the relation between this phenomenon and problem of the rate of the purification of wastewater.

The aim of this work is the study of the self-organization and physicochemical properties of solutions of **1** in a range of concentrations of 10^{-4} – 10^{-12} mol/L, establishing a relationship between the concentration dependence of the parameters nanoassociates, physicochemical properties of the solution **1** and the rate of the purification of wastewater. It was shown that aqueous solutions of **1** are self-organizing system in which nanoparticles are formed. The size and zeta- potential of nanoassociates in different intervals of a concentration of **1** are substantially different. The aggregates (50 nm) and the nanoassociates (200-100 nm) are formed in range of concentrations 10^{-5}-10^{-4} mol/L and 10^{-12}-10^{-6} mol/L, considerably. The difference in the parameters of nanoparticles formed in "normal" and low concentrations is the most probable cause of a change of the rate of purification process of wastewater in presence of **1** in various ranges of concentrations.

References

[1]. A. I. Konovalov, I. S. Ryzhkina, L. I. Murtazina, A. P. Timosheva, R.R. Shagidullin, A.V. Chernova, L. V. Avvakumova, and S.G. Fattakhov// Russian Chemical Bullrtin, International Edition, 2008, Vol. 57, No. 6, pp. 1231-1238.

[2]. I. S. Ryzhkina, L. I. Murtazina, Yu. V. Kiseleva, and Academician A. I. Konovalov// Doklady Physical Chemistry, 2009, Vol. 428, Part 2, pp. 196–200.

Acknowledgements

This work was supported by RFBR (№ project 10-03-00147).

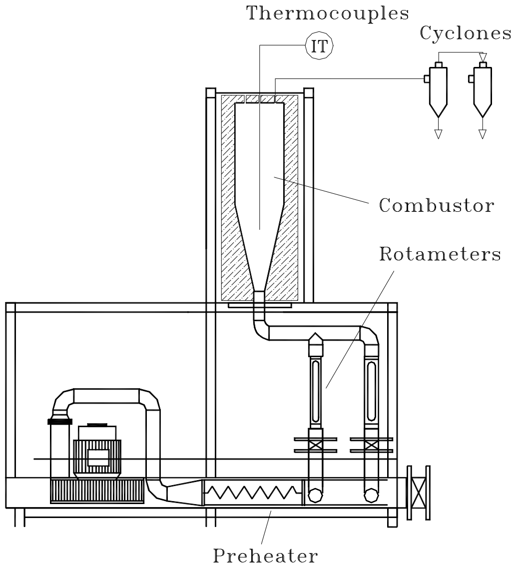
PP-III-60

DESIGN OF CONICAL SPOUTED BED COMBUSTOR FOR VALORIZATION OF CORK STOPPER WASTES

María J. San José, **Sonia Alvarez, Luis B. López, Martin Olazar and Javier Bilbao**

Departamento de Ingeniería Química, Facultad de Ciencia y Tecnología,
Universidad del País Vasco, Aptdo 644. 48080 Bilbao. Spain.
Tel: 34-94-6015362. Fax: 34-94-6013500 e-mail: mariajose.sanjose@ehu.es

Renewable biomass sources are of growing importance in satisfying energy needs over fossil fuels. In 2007, near 10.000 million stoppers made of cork wastes ended up landfilled. As cork has a high heating value, it is suitable for energy production. Combustion in fluidized beds of cork with inert material produces VOCs and PAHs emissions [1]. Suitability of the spouted bed technology for thermal valorization of biomass by combustion [2-4] has been proven without inert material, due to the capacity for handling large size particles, of irregular texture, with a wide size distribution and sticky solids as cork stoppers [5-6]. In this paper, an experimental unit at pilot plant scale. Figure, has been used for combustion of cork wastes and the optimal design of the conical spouted bed combustor has been determined. The study has been carried out with beds consisting of cork wastes, of density ρ_s= 270 kg/m^3 and of average Sauter diameter between 5 and 25 mm.



The results prove the optimal design of the conical spouted bed combustor for successful combustion of cork wastes.

References

[1]. Cabañas, A., Saez, F., González, A., Escalada, R., 2000. J. Agric. Engng. Res., 77 (3), 349.
[2]. San José, M.J., Aguado, R., Alvarez, S. Olazar.M., 2002. Inform. Tecnol., 13(2), 127.
[3]. San José, M.J., Álvarez, S., Ortiz de Salazar, A., Olazar, M., Bilbao, J. Science in Thermal and Chemical Biomass Conversion, Newbury Berks, UK: CPL press. vol. 1, 228-236(2006).
[4]. San José, M.J., Alvarez, S., Ortiz de Salazar, A., Morales, A., Bilbao, J., 2006. Int. J. Chem. React. Eng., 4, A15, 1.
[5]. Olazar, M.; San José, M.J.; Peñas, F. J.; Bilbao, J., 1994. Ind. Eng. Chem. Res., 33, 1838.
[6]. Olazar, M., San José, M.J., LLamosas, R., Bilbao, J., 1994. Ind. Eng. Chem. Res,. 33: 993.

Acknowledgements

This work was carried out with the financial support of the University and the County Council of Biscay (Project DIPE 07/09) and of Spanish Ministry of Science and Innovation (Project TRA2009-0318).

BIODIESEL FROM MICROALGAE OIL PRODUCTION IN TWO SEQUENTIAL ESTERIFICATION/TRANSESTERIFICATION REACTORS: PINCH ANALYSIS OF HEAT INTEGRATION

Eduardo Sánchez[1], **Karina Ojeda**[1], **Viatcheslav Kafarov**[1],
Mahmoud El-Halwagi[2]

[1]*Industrial University of Santander, Bucaramanga, Colombia,*
sancheztuiran@gmail.com
[2]*Texas A&M University, College Station, Texas, USA*

Biodiesel production from non-edible sources have been extensively studied [1-5]. As biodiesel is obtained by means of the transesterification of the triglycerides of the oils, there are some cases in which the high content of free fatty acids makes the oil too acid making the basic transesterification no longer the best alternative. Such cases are quite frequent when waste vegetable oils (WVO's) are used as raw material or when new non-edible high-acidic value oil sources, like microalgae oil, are used. In such cases, before the basic transesterification takes place there is the possibility to esterify the free fatty acids of the oil, so fatty acid alkyl esters and water are obtained and separated, so then the basic transesterification of the triglycerides will take place more conveniently [6].

To achieve this sequential design, some heat transfer operations must been performed in order to increase the production and quality of the desired products. So, in this work, a heat integration by means of a pinch analysis of the process streams is made in order to reduce both the external heating and cooling services. Energetic requirements with and without heat integration are compared. Aspen Plus 2006.5^{TM} software is used to simulate the esterification-transesterification process. The microalgae *C. Vulgaris* oil is used as raw material for the biodiesel production. Data according to microalgae oil composition and properties were obtained from literature [7]. Finaly we will discuss about several alternatives in order to improve the energetic efficiency of the process.

References

[1]. Al-Widyan MI, Al-Shyoukh AO. Experimental evaluation of the transesterification of waste palm oil into biodiesel. Bioresour Technol **2002**;85:253–6.

[2]. Al-Widyan MI, Tashtoush G, Abu-Qudais M. Utilization of ethyl ester of waste vegetable oils as fuel in diesel engines. Fuel Process Technol **2002**;76:91–103.

[3]. Cayh G, Selim K. Increased yields in biodiesel production from used cooking oils by a two step process: Comparison with one step process by using TGA. Fuel Process Technol **2008**;89(2):118–22.

[4]. Costa Neto PR, Rossi L, Zagonel G, Ramos L. Producao de Biocombustivel Alternativo ao Oleo Diesel Atraves da Transesterificacao de Oleo de Soja Usado ern Frituras. Quim Nova **2000**;23:531–7.

[5]. Dorado MP, Ballesteros E, Arnal JM, Gomez J, Lopez FJ. Exhaust emissions from a diesel engine fuelled with transesterified waste olive oil. Fuel **2003**;82:1311–5.

[6]. Marchetti JM, Errazu AF. Esterification of free fatty acids using sulfuric acid as catalyst in the presence of triglycerides. Biomass Bioenergy **2008**;32:892–5.

[7]. Petkov G and Garcia G. Which are fatty acids of the green alga *Chlorella*? Biochem. Sys. and Ecol. **2007**; 35: 281-5.

Acknowledgements

The authors wants to express their gratitude to the Industrial University of Santander and to the Texas A&M University for their financial support.

DEVELOPING MICROFLUIDIC DEVICE WITH EMBEDDED NANOSTRUCTURES FOR IN-SITU RAMAN OPERANDO SPECTROSCOPY

Victor Sans[1], **Vladimir Kozhevin**[2,3], **Denis Yavsin**[2,3], **Igor Kuzmin**[2],
Sergey Gurevich[2,3], **Alexei Lapkin**[1]

[1]School of Engineering, University of Warwick, United Kingdom,
V.Sans.Sangorrin@warwick.ac.uk
[2]INCATTECH LLC, St. Petersburg, Russia
[3]Ioffe Physical Technical Institute, Russian Academy of Sciences, Russia

Microfluidic devices have gained importance over the last years in chemical synthesis, biological and analytical applications.[1-3] The coupling of microfluidic devices with in-situ spectroscopic techniques capable to provide analytical information about the reaction media opens a new whole set of opportunities to study and optimise chemical kinetics, reaction mechanisms, thermodynamic properties of interest, etc.[4-5] The simultaneous spectroscopic characterization of a catalytic material during the reaction and the measurement of its catalytic activity/selectivity has been coined as Operando Spectroscopy.[6]

Herein, we report on the application of laser electrodispersion (LE) to deposit amorphous gold nanoparticles (AuNPs) with a narrow size distribution on the Si and SiO_x surfaces (Figure 1). The particles were deposited on etched and oxidized Si wafers and studied by TEM, SEM and XPS. Their application in surface enhanced Raman spectroscopy (SERS) is described using methylene blue and crystal violet as target molecules (Figure 2). The AuNPs proved to be efficient to detect very low concentrations of analytes (10^{-8} M).

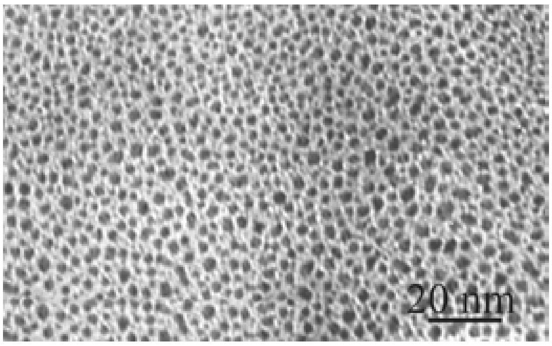


Figure 1. TEM image corresponding to AuNPs deposited by laser electrodeposition.

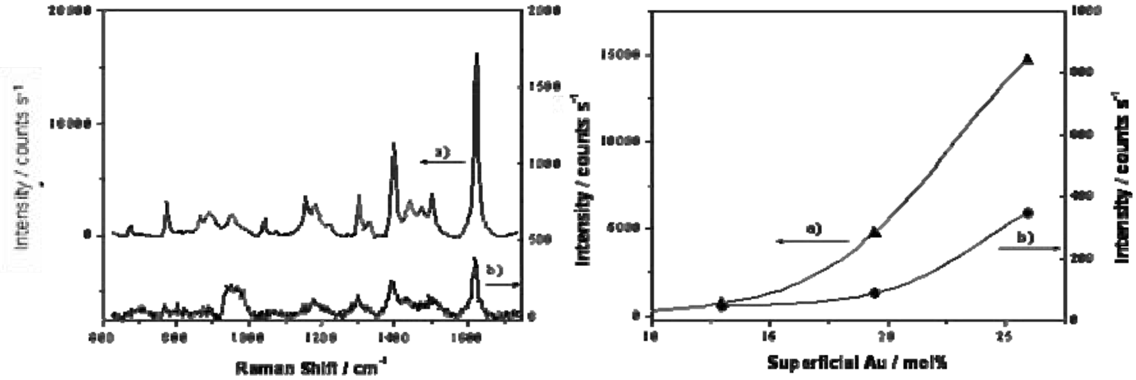


Figure 2. SERRS spectra (left) and the intensity of 1625 cm^{-1} band of MB adsorbed on gold nanoparticles as a function of the amount of Au deposited (right). (a) Au/SiO$_x$ and (b) Au/Si samples.

In a second stage, the AuNPs were deposited on the bottom of microchannels etched in Silicon wafers. The channels were closed with glass using anodic bonding and commercial adhesives (Figure 3).The suitability of these systems to be used as continuous-flow SERS cells was studied.

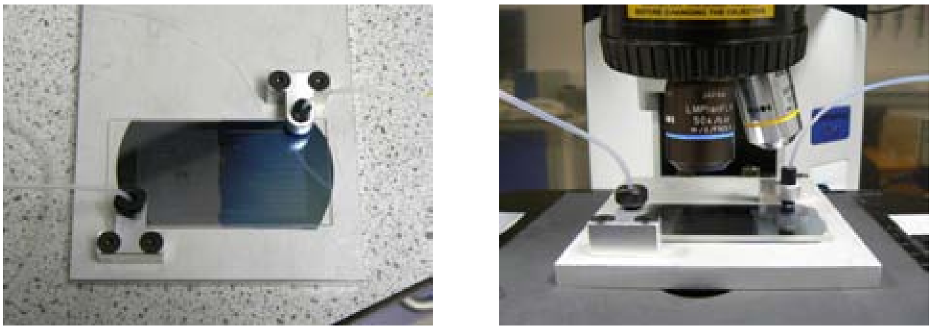


Figure 3. Left picture: Glass-Silicon microreactor with AuNPs deposited on the channels. Right picture: Continuous-flow SER(R)S experimental set-up.

References

[1]. B. P. Mason, K. E. Price, J. L. Steinbacher, A. R. Bogdan, D. T. McQuade, *Chem. Rev.*, **2007**, 107. 2300-2318.

[2]. E. W. K. Young, D. J. Beebe, *Chem. Soc. Rev.,* **2010**, 39, 1036-1048.

[3]. L. Tong, M. Righini, M. U. Gonzalez, R. Quidant, M. Kall, *Lab Chip*, **2009**, 9, 193-195.

[4]. R. Herzig-Marx, K. T. Queeney, R. J. Jackman, M. A. Schmidt, K. F. Jensen, *Anal. Chem.*, **2004**, 76, 6476-6483.

[5]. A. Urakawa, F. Trachsel, P. R. von Rohr, A. Baiker, *Analyst*, **2008**, 133, 1352–1354.

[6]. M. A. Bañares, *Catal. Today*, **2006**, 100, 71-77.

Acknowledgements

EPSRC is gratefully acknowledged for funding.

THREE-PHASE DIRECT OILS HYDROGENATION

<u>Shtertser N.V.</u>, Minyukova T.P., Filonenko G.A., Khassin A.A.

Boreskov Institute of Catalysis SB RAS, Prosp. Akad. Lavrentieva, 5, 630090,
Novosibirsk, Russia, Fax: +7-383-3308056; E-mail: nat@catalysis.ru
Novosibirsk State University, ul. Pirogova, 2, 630090, Novosibirsk, Russia
Fax: +7-383-3302237

Three-phase hydrogenation is one of the most effective ways of vegetable oil processing to produce fatty alcohols and hydrocarbons. Using copper containing catalysts in the process of oil hydrogenation may be prospective because of its high activity in hydrogenation reactions. It is well known that copper containing catalysts activity and selectivity strongly depends on catalyst precursor composition and structure, despite metallic copper particles are the active sites. Each catalyst is efficient in a peculiar hydrogenation process: Cu-Zn containing catalysts with wurtsite-like structure in methanol synthesis, Cu-Si containing with chrysocolla structure in hydrogenation of lactic acid to propanediol, copper chromite – in ketone hydrogenation to alcohols.

Fatty acids triglycerides hydrogenation was carried out under pressure 2MPa in the temperature range of 280-340°C using model catalysts which structures were thoroughly studied earlier: copper hydrosilicate ($(Cu,H)_2[Si_2O_5](OH)_4$ chrysocolla) [1], copper chromite ($CuCr_2O_4$ tetragonal distorted spinel) [2] and a solid solution of Cu^{2+} in ZnO ((Cu,Zn)O wurtzite-like structure) [3].

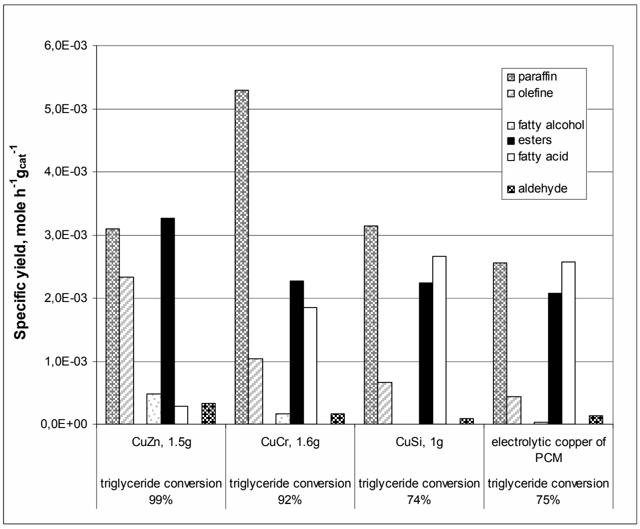


Figure 1. Products distribution in the reaction of triglyceride hydrogenation. T_r=340°C, initial triglyceride volume 21ml, reaction time 3h, hydrogen velocity 7l/h, P_{H2}=2MPa

Our results allow supposition that hydrogenation of an ester group of triglycerides occurs by three routes, which give (1) (ester of fatty acid and 1,2-propanediol) + fatty acid; (2) diglyceride + fatty alcohol; (3) diglyceride + aldehyde.

The following steps are hydrogenation of acids to alcohols and further – to hydrocarbons. Also, esterification reactions result in C_{18}-C_3 and C_{18}-C_{18} esters formation.

(Cu,Zn)O catalyst was found to

be the most efficient of catalysts studied; however its activity in the hydrogenation of OH groups and double bonds was less than that of $CuCr_2O_4$ sample. $(Cu,H)_2[Si_2O_5](OH)_4$ catalyst was found to be much less active in comparison to the patterns of $CuCr_2O_4$ and (Cu,Zn)O.

There is some correlation of catalytic properties of investigated catalysts and data on kinetics of its reduction.

The results showed [2,3] that copper ions reduction of $CuCr_2O_4$ and (Cu,Zn)O catalysts occurs without removal of lattice O^{2-} anion according to the reaction $Cu^{2+} + H_2 \rightarrow Cu^0 + 2H^+_{abs}$. The generated protons are absorbed by the oxide structure in the form of OH^- and HOH groups. $(Cu,H)_2[Si_2O_5](OH)_4$ catalyst reduction occurs according to traditional mechanism with water formation.

Kinetics parameters of copper cations reduction was calculated according to Ozawa-Flynn-Wall method using experimental thermal curves DSC of reduction in hydrogen. The results presented in Table 1 reveal that activation energy of reduction of just calcined at 250-350°C catalysts $CuCr_2O_4$ and (Cu,Zn)O in 2-3 time higher comparing to other investigated catalysts.

Table 1. Kinetic parameters of copper cations reduction in hydrogen. Two values correspond to parameters at low conversion (~ 10 %) and high conversion (~ 80 %) of copper.

Sample	E_a, kJ/mole	$\log(k_0(sec^{-1}))$	supposed mechanism
$(Cu,H)_2[Si_2O_5](OH)_4 \cdot nH_2O$	$47 \rightarrow 41$	$2.2 \rightarrow 5.2$	With O^{2-} removing and water formation
$Cu_{0.08}Zn_{0.92}O$ (air exposed)	$46 \rightarrow 64$	$2.1 \rightarrow 2.6$	
$Cu_{0.08}Zn_{0.92}O$(just calcined)	$100 \rightarrow 130$	$10.3 \rightarrow 14.5$	With H^+ absorption in the form of OH^- и HOH groups in oxide structure
$CuCr_2O_4$	$99 \rightarrow 121$	-	

The results of investigation of catalytic and physicochemical properties of copper containing catalysts may allow us to create bicatalytic permeable composite monolith to combine best activity in reaction of hydrogenolysis of ester groups with best activity in the reaction of hydrogenation of fatty acids and double bonds to produce fatty alcohols and hydrocarbons from vegetable oils.

[1]. T.M.Yurieva, et al., Mater. Res. Innov., 5 (2), 74-80, (2001).
[2]. A.A. Khassin, et al., VIII Int. Conf. on Mechanisms of Catal. React. (MCR-VIII), 29 июня-2июля, 2009, Novosibrisk.
[3]. A.A. Khassin, et al., Physical Chemistry Chemical Physics, 11, 6090 – 6097, (2009).

Co-BASED CATALYSTS FOR THE HYDROLYSIS OF BOROHYDRIDES TO GENERATE PURE HYDROGEN FOR PEM FUEL CELL

Simagina V.I.[a], Netskina O.V.[a], Komova O.V.[a], Kellerman D.G.[b], Odegova G.V.[a]

[a]Boreskov Institute of Catalysis SB RAS, Pr. Akademika Lavrentieva 5,
Novosibirsk, 630090, Russia, simagina@catalysis.ru
[b]Institute of Solid State Chemistry UB RAS, Pervomaiskaya Street 91,
Ekaterinburg, 620219, Russia

Hydrogen storage is today one of the most important issues that hinders the development of a hydrogen economy. Many studies searching for effective storage materials are in progress but none has reached the technical criteria that could make them viable from the technological and commercial points of view. According to many researchers, hydrogen generators based on hydrolysis of hydrides are offered as promising portable devices that were employed with proton-exchange fuel cells. Among the hydrides, sodium borohydride (10.5 wt% H) and ammonia-borane (19.4 wt% H) are desirable due to high hydrogen content and the high stability [1, 2].

The works of catalysts development for portable hydrogen generators were begun at the end of 90s. [1-4] In the most cases, the high level of H_2 generation is reached by high loading of noble metal and catalysts quantity. Today, most of the published papers about the $NaBH_4$ and NH_3BH_3 hydrolysis deal with improvement of catalytic materials [3,4]. The most efficient metals (supported or not) are the noble metals. A non-noble metal, cobalt, has showed promising catalytic performances and many studies have then focused on improving its performances. Also for reactor development (the portable hydrogen generator) still remain unsolved problems of the creation of macrostructured catalysts in the form of granules and blocks needed for the flow operation.

A series of supported catalysts were prepared by impregnation method using aqueous solutions of Pt, Pd, Ru, Rh, Co, Ni compounds. The following materials were used as supports: carbon material «Sibunit», γ-Al_2O_3, several samples of TiO_2 (anatase); $LiCoO_2$ and Ni form. Catalysts were reduced in a reaction medium of hydride. The process of $NaBH_4$ and NH_3BH_3 hydrolysis was carried out at 20-50°C in a glass temperature-controlled internal mixing reactor as described [5]. Catalysts were studied by different methods: magnetic susceptibility measurement, XRD, FTIR, DRS, TEM, SEM, EXAFS-XANES, XPS.

Hydrogen generation processes from $NaBH_4$ and NH_3BH_3 have been studied in the presence of different nanoscale (supported or not) catalysts containing Pt, Ru, Rh, Co, Ni. By varying the conditions of the catalyst preparation and the nature of the active component and support it was possible to control the properties of the hydrogen-generating systems and the rate of the processes. Low cost and catalytically effective cobalt catalysts are very attractive in developing on-demand hydrogen generation system for practical application. Different cobalt salts ($CoCl_2$, $Co(NO_3)_2$, $Co(CH_3COO)_2$), cobalt hydroxide and Co_3O_4) were investigated as catalytic materials for the borohydride hydrolysis. During the investigation, it was found that cobalt-based catalysts are being reduced in the reaction media of $NaBH_4$ hydrolysis to form the active ferromagnetic phase. Ferromagnetic property of the cobalt-based catalyst makes it convenient for being recycled from reaction products and allows designing new type of catalytic reactors for portable applications. The data of magnetic susceptibility investigation indicated that new active phase consist of cobalt borides. Data of the study of dependence of the catalytic samples magnetic susceptibility values on temperature lead to conclusion that active catalytic phase is Co_2B. Moreover catalytic samples prepared from Co_3O_4 are characterized with high magnetic susceptibility value and high level catalytic activity.

It was showed that the rector of portable generator can be supplied by structured catalyst .Methods of macrostructured catalysts preparation have been developed. Using cobalt borides supported on Ni-foam allows to achieve next advantages: strength support, low hydrodynamic and aerodynamic resistance, easy separation of spent solutions.

The authors are thankful to the RFBR (grants № 09-08-00505-a и № 09-08-00546-a) for the financial support.

REFERENCES

[1]. S.C. Amendola, S.L. Sharp-Goldman, M.S. Janjua, M.T. Kelly, P.J. Petillo, M. Binger, J. Power Sources, 85 (2000) P. 186.

[2]. Y. Kojima, K. Suzuki, K. Fukumoto, M. Sasaki, T. Yamamoto, Y. Kawai, H. Hayashi, Int. J. Hydrogen Energy, 27 (2002) P. 1029.

[3]. V. Sumerin, F. Schulz, M. Nieger, M. Atsumi, C. Wang, M. Leskelä, P. Pyykkö, T. Repo, B. Rieger. J. Organomet. Chem. 2009. Vol. 694. P. 2654.

[4]. B.H. Liu, Z.P. Li. J. Power Sources. 2009. Vol. 187. P. 527.

[5]. V.I. Simagina, P.A. Storozhenko, O.V. Netskina, O.V. Komova, G.V. Odegova, Yu.V. Larichev, A.V. Ishchenko, A.M. Ozerova. Catalysis Today. 2008. Vol. 138. P. 253.

PP-III-65

KINETIC STUDY OF THE CATALYTIC TRANSFORMATION OF BIOMASS COMPONENTS OVER GOLD CATALYSTS

Olga A. Simakova[1], Yulia S. Solkina[2], Päivi Mäki-Arvela[1], Irina L. Simakova[2]

[1]*Åbo Akademi University, Turku/Åbo, Finland, E-mail: dmurzin@abo.fi*
[2]*Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia*

There is a great interest to use biomass as a feedstock for fine chemicals. Linoleic acid and α-pinene derived from wood attract an interest as a source for production of valuable compounds applied as pharmaceuticals and fragrances [1]. These transfotmations are achieved via C=C double bond isomerization reaction (Figure 1). The valuable product of linoleic acid isomerization – conjugated linoleic acid (CLA) is produced industrially applying homogeneous catalysis in the batch mode, which have several drawbacks, such as utilizing of large amount of organic solvents, inorganic alkali and acid. These shortcomings can be overcome by applying heterogeneous catalysts and as a next step of this process developing – shifting to the continuous operation. However, are only few papers reported application of heterogeneous catalysts for isomerization with ruthenium, silver and gold as active components [2-4]. The most selective catalyst for this process is gold.

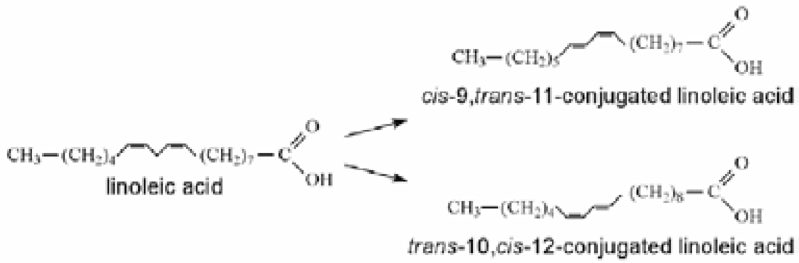


Figure 1. Isomerization of linoleic acid to conjugated linoleic acids.

The desired product of α-pinene isomerization is camphene, which is synthesized in industry over titania oxide activated by H_2SO_4. The selectivity is not exceeding 50%, while application of gold catalyst is allowed to increase the selectivity up to 90-96%. The kinetics of this process is not studied until now. Thus, understanding of kinetic parameters and development of α-pinene isomerization to camphene over gold catalyst is needed.

In the first part of this study isomerization of linoleic acid was carried out in a semi-batch reactor. In this system the gas (hydrogen) was flown continuously through the liquid phase (linoleic acid in *n*-decane) and the heterogeneous gold catalysts were used. The example of kinetic curves is shown on Figure 2.

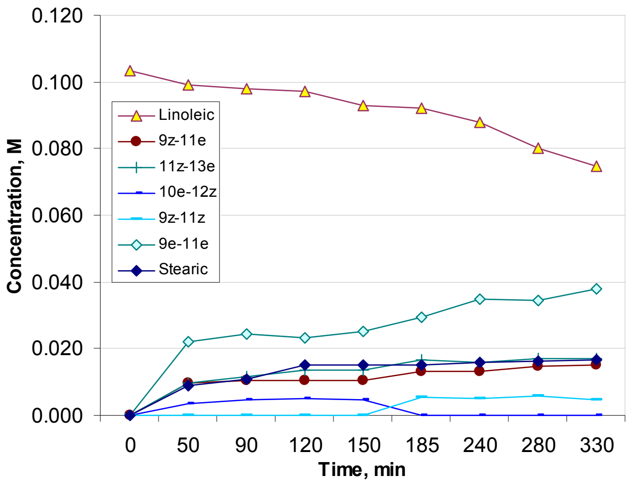


Figure 2. Isomerization of linoleic acid to CLA at 423K, over Au/SiO_2 in semi-batch reactor under hydrogen and nitrogen flow. Conversion after 5.5 h is 28%. Selectivity towards hydrogenation is 18%, selectivity to isomerization is 82%.

During the process both: hydrogenation and isomerization occured. Changing of catalysts allowed to vary activites and selectivities. The influence of mass transfer limitations was verifie by changing the catalyst mass, stirring speed and particle sizes. To shift from a batch to continuous reactor operation more detailed kinetic studies are needed for isomerization reactons. Taking into account physicochemical properties of the fluid phase, deactivation and mass transfer, α-pinene isomerization over gold catalyst in continuous reactor was performed. The scheme of the utilized continuous reactor is presented on the Figure 3.In our study investigation of kinetic parameters, such as rate constants, activation energy, reaction orders, concentration profiles depending on time-on-stream and catalyst deactivation using gold as a catalyst was done.

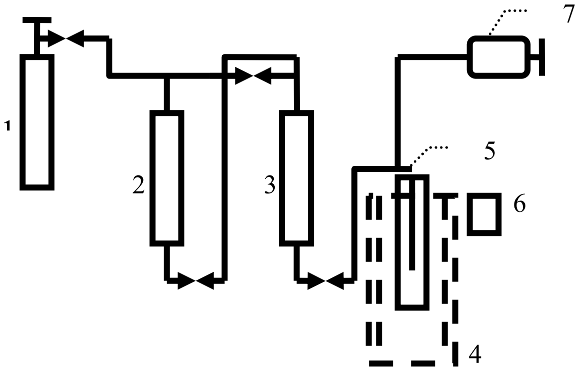


Figure 3. Scheme of set-up for α-pinene vapour-phase isomerization: 1 – H_2, 2 - Ni-Cr catalyst, 3 – SiO_2, 4 – oven, 5 – reactor, 6 – sample colector, 7 – solution of α-pinene.

References

[1]. I.L. Simakova, Yu. Solkina, I. Deliy, J. Wärnå, D.Yu. Murzin, Appl. Catal. A.: Gen., 356 (2009) 216.

[2]. A. Bernas, P. Lukkanen, N. Kumar, P. Mäki-Arvela, J. Väyrynen, E. Laine, B. Holmbom, T. Salmi, D.Yu. Murzin, J. Catal., 210 (2002) 354.

[3]. M. Kreich, P. Claus, Ang. Chem., Int. Ed. 44 (2005) 7800.

[4]. O.A. Simakova, A.-R. Leino, B. Campo, P. Mäki-Arvela, K. Kordás, J.-P. Mikkola, D.Yu. Murzin, Catal. Today, 150 (2010) 32.

PRODUCTION OF HYDROGEN AND NANOFIBROUS CARBON BY SELECTIVE CATALYTIC PYROLYSIS OF LIGHT HYDROCARBONS ON BIMETALLIC Ni-CONTAINING CATALYSTS

Solovyev E.[1], **Ermakov D.**[2], **Kuvshinov G.**[1]

[1]*Novosibirsk State Technical University, K. Marx Pr-t 20, Novosibirsk 630092, Russia*
e-mail: gennady.kuvshinov@gmail.com
[2]*Boreskov Institute of Catalysis SB RAS, Lavrentiev Pr-t 5, Novosibirsk 630090, Russia*

Hydrogen is important chemical and perspective energy carrier for hydrogen energetics. The main problem in successful development of hydrogen energetics is relatively high cost of hydrogen produced by conventional steam reforming of methane (natural gas). This method is based on multi-step process including catalytic conversion of methane and water to synthesis gas ($CO+H_2$), water-gas shift reaction to convert CO into CO_2 and CO_2 removing. Complexity and necessity of hydrogen purification determine high operating costs, especially for production of hydrogen for small proton exchange membrane fuel cell (PEMFC) power plants. Moreover even very small impurities of CO (>30 ppm) could damage PEMFC.

Direct non-oxidative catalytic pyrolysis of hydrocarbons into hydrogen and nanofibrous carbon (NFC) is alternative one-step process to produce CO-free hydrogen. This process is effectively carried out by using Ni-based catalysts at temperatures 400–700°C with producing hydrogen and methane as the main gaseous products [1]. Due to thermodynamic there is quite low $H_2:CH_4$ ratio at given conditions. To produce H_2–CH_4 mixtures with more than 50 vol.% of hydrogen the process of hydrocarbon decomposition should be carried out at the temperatures above 700°C or be accompanied by separation of methane from the reaction products that is quite complicated technical problem. Increase of process temperature result in increase of energy consumption and can cause rapid catalyst deactivation by carbons deposited on active catalytic sites. At the same time oxidative catalyst regeneration is unprofitable because of loss of a valuable NFC product.

It is known that addition of second metal in Ni-containing catalyst can improve its activity and lifetime [2]. At that conversion of initial hydrocarbon is raised and as a result hydrogen yield could be increased. Further more it has been ascertained that use of hydrocarbons heavier than CH_4 as a feedstock such as C_3H_8 allows to increase the selectivity of hydrogen and reduce the concentration of CH_4 in gaseous products almost to the zero-level [3]. This circumstance has a great practical importance due to the fact that H_2 could be easier separated from C_2-C_4 hydrocarbons than CH_4 (e.g. by relatively inexpensive membrane separation).

The present work is devoted to studies of non-traditional process of hydrogen production by selective catalytic pyrolysis of C_2-C_4 hydrocarbons which proceeding in non-equilibrium manner. High-loaded bimetallic Ni-M/SiO_2 (M=Cu, Mo, Co, Fe) catalyst with total metal content of 90 wt.% and SiO_2 as textural promoter were used. Experiments were carried out in quartz flow reactor with a vibrofluidized bed under atmospheric pressure at 550–650°C using undiluted propane, butane, ethylene and propane-butane mixture (commercial LPG) as a feedstock.

As a result influence of operating conditions (hydrocarbon, catalyst composition and temperature) on hydrogen yield and selectivity, as well as some textural and structural properties of carbon nanofibers was established. The possible mechanism of the process of catalytic pyrolysis of C_2-C_4 hydrocarbons included intermediate steps of formation of active surface species is suggested for explanation the effects observed.

For instance hydrogen concentration in reaction products in the process of pyrolysis of C_3H_8 on 50 wt.% Ni-40 wt.% Cu/SiO_2 catalyst at 600°C reaches up to 60 vol. %. At the same time the H_2:CH_4 ratio not less than 12:1 could be achieved during more than 20 hours. After removal of C_2-C_4 hydrocarbons from reaction products by conventional inexpensive method (e.g. separation using inorganic membrane) one can receive CO-free mixture of hydrogen and methane containing more than 95 vol.% of hydrogen. This mixture is suitable as a fuel for PEMFC without any additional processing.

References

[1]. Chouldhary T.V., Goodman D.W. CO-free fuel processing for fuel cell applications. // Catalysis Today, N77, 2002, p. 65-78.

[2]. Shah N., Panjala D., Huffman G.P. Hydrogen production by catalytic decomposition of methane. // Energy & Fuels. - 2001. N. 15, 2001. - P. 1528-1534.

[3]. E.A. Solovyev, D.G. Kuvshinov, D.Yu. Ermakov, G.G. Kuvshinov Production of hydrogen and nanofibrous carbon by selective catalytic decomposition of propane // Int. J. Hydrogen Energy – 2009. V. 34 (3). – P. 1310.

Acknowledgements

This work was financially supported by programs of Ministry of education and science of the Russian Federation: “Research and educational staff of innovative Russia” (contract 02.740.11.0053) and “Development of scientific potential of the higher school” (contract 2.1.1/1758).

PP-III-67

ENHANCED GASIFICATION OF PHYSIC NUT WASTE OVER SOL-GEL DERIVED $La_{1-x}Ce_xNiO_3$ PEROVSKITE CATALYST

Kanit Soongprasit[1,2], Duangdao Aht-Ong[1,2],
Viboon Sricharoenchaikul[3], and Duangduen Atong[4]

[1]Department of Materials Science, Faculty of Science, Chulalongkorn University, Bangkok, 10330, Thailand
[2]Research Unit of Advanced Ceramics and Polymeric Materials, National Center of Excellence for Petroleum, Petrochemicals and Advanced Materials, Chulalongkorn University, Bangkok, 10330, Thailand
[3]Department of Environmental Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok, 10330, Thailand
[4]National Metal and Materials Technology Center, Thailand science Park, Pathumthani, 12120, Thailand, duangdua@mtec.or.th

Perovskite-type mixed oxides $La_{1-x}Ce_xNiO_3$ (x=0, 0.2, and 0.4) were prepared by sol-gel method with polyvinyl alcohol (PVA) as gelating agent. Sol-gel method usually reported with smaller particle size, low agglomeration and low process temperature [1]. The as-prepared catalyst were calcined at 800 °C for 5 hrs. Effects of Ce substituted La on crystal structure and morphology of perovskite catalyst were investigated. Crystal structure characterized by XRD showed peak characteristics of $LaNiO_3$ at all condition and CeO_2 phase when Ce was added into catalyst precursors without $La(OH)_3$, the intermediate phase during $LaNiO_3$ transformation, as show in Figure 1. The greater Ce substitution was confirmed by the increase of CeO_2 peak intensity. Moreover, NiO peak intensity increased with Ce substitution because of oxidation of Ni ion during calcination. Introduction of Ce tended to decrease crystal size of perovskite catalyst from 14.35 nm to 12.33 nm while increase surface area to almost 2 times (Table. 1). SEM images displayed homogeneous dispersion of catalyst particles prepared by sol-gel method with low agglomeration.

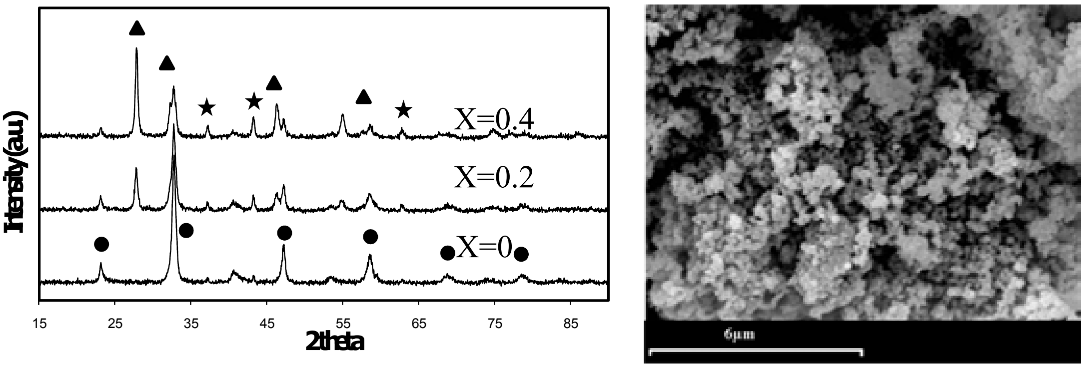


Figure 1. (a) XRD pattern of synthesized $La_{1-x}Ce_xNiO_3$ (x=0, 0.2 and 0.4) (● $LaNiO_3$, ▲ CeO_2, ★ NiO), (b) SEM images of $La_{0.6}Ce_{0.4}NiO_3$ catalysts

Particle size and specific surface area of these catalyst were in the range of 13.85-16.70 µm and 5.08-9.36 m^2/g respectively. EDS mapping technique reported homogeneous dispersion of La and Ce on the surface.

Activity of prepared catalyst was carried out with laboratory-scale gasifier using physic nut waste as raw materials at 700°C and 800°C (Figure 2). Online TCD-NDIR gas analyzer indicated that the main gaseous products from gasifying process is CO_2, CO, H_2, and C_xH_y. In addition, significant amount of condensable organic compound (tar) was converted to favorable permanent fuel gas by prepared catalyst. $La_{0.8}Ce_{0.2}NiO_3$ catalyst exhibited highest activity at 800°C with carbon conversion of 60%. Addition of Ce can enchanced oxygen storage and mobility on the surface of catalayst [2] which resulted in superior hydrocarbon cracking performance. Long term stability test of the perovskite catalyst was also carried out for 24 hours with negligible change in catalytic activity in term of quality and quantity of gas production.

Table 1. Characteristics of perovskite-catalyst.

Catalyst	Crystal size (nm)	Particle size (µm)	Specific surface area (m^2/g)
$LaNio_3$	14.35	16.70	5.08
$La_{0.8}Ce_{0.2}NiO_3$	14.69	16.37	7.06
$La_{0.6}Ce_{0.4}NiO_3$	12.33	13.85	9.36

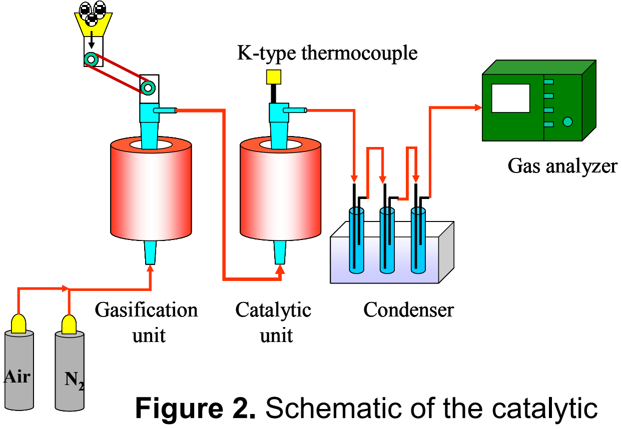


Figure 2. Schematic of the catalytic gasification system setup

References

[1]. A.J Zhou et al. Fabrication and thermoelectric properties of perovskites-type oxide $La_{1-x}Sr_xCoO_3$. Journal of Alloys and Compounds, 449, 2007, 105-108.

[2]. Cui, Y. et al. Steam reforming of glycerol: The experimental ativity of $La_{1-x}Ce_xNiO_3$ catalyst in comparison to thermodynamic reaction equilibrium. Applied Catalysis B,90, 2009, 29-37

Acknowledgements

This research was supported by the National Metal and Materials Technology Center (Project No. MT-B-52-CER-07-249-I). K.Soongparsit thanks The Chulalongkorn University Graduate Scholarship to Commemorate the 72nd Anniversary of His Majesty King Bhumibol Adulyadej and The Research Unit of Advanced Ceramics and Polymeric Materials for financial support.

INFLUENCE OF SPILLOVER ON EQULIBRIUM COVERAGE OF SUPPORTED Pt NANOPARTICLES BY CARBON MONOXIDE: MONTE CARLO SIMULATION

Stishenko P.V.[1], **Myshlyavtsev A.V.**[1,2]

[1]*Omsk State Technical University, Russia, pvstishenko@omgtu.ru*
[2]*Institute of Hydrocarbons Processing SB RAS, Omsk, Russia*

Enhanced catalytic activity of metallic nanoparticles (NP) was initially discovered for Au in 1989 and stimulated numerous researches in this area. Since then a significant progress has been archived in explanation of this phenomenon. Also many other interesting properties of NP were found. Today NP are used in vast majority of modern catalysts and considered to be applied in electronics, photonics, medicine, data storage devices, chemical sensors and *etc*. According to modern notion, peculiar properties of NP can be explained with presence of different kinds of metal faces, including high index ones and with different surfaces defects such as vacancies, steps and kinks. Influence of a support via spillover effect also recognized to be significant for some reactions and processes [1].

Despite progress in this field, a complete computer model still exists neither for catalytic processes nor even for adsorption-desorption processes on NP surface. There are numerous experimental and computer simulation researches dedicated to investigation of equilibrium shape of NP. Many approaches and algorithms exist for simulation of adsorption of heterogeneous bulk surfaces [2]. With DFT approach simple reactions on NP surface can be investigated [3] but this method is too computationally expensive to be used with realistic size nanoparticles (hundreds and thousands of atoms).

We propose a model of adsorption on supported metallic NP which takes into account possible changes of NP shape such as variation of relation of face types squares and formation of above mentioned surface defects in a limit of lattice representation. For description of adsorption an explicit tying to some definite local configuration of surface atoms is used. This allows simulation of multiple adsorption site types described in a manner compatible with existing data about adsorption energy known from experimental works and from computations with lower approximation level, i.e. molecular dynamics and DFT. Influence of a support via spillover effect can be simulated using special adsorption sites on a support.

Using the proposed model we have found thermodynamically equilibrium shape of Pt NP located on an abstract support with the same lattice. Parameter values for Pt-Pt interactions were taken from work [4]. These data were used in many simulation researches and proved to be enough realistic. Interactions between NP and support were fitted to make particle shape matching to TEM images.

For obtained nanoparticles Monte Carlo simulations of carbon monoxide (CO) adsorption-desorption processes were performed. Seven adsorption site types were considered in simulations: atop, bridge, fcc-hollow and hcp-hollow on (111) face; atop, bridge and hollow on (100) face. CO adsorption energies were taken from [5-6] where they were obtained from DFT simulations. To investigate an influence of spillover effect on NP coverage we introduced atop adsorption sites on support surface. Diffusion of adsorbed CO molecules was fast enough fast to equilibrate distribution over surface and particle either in case of infinitely far diffusion steps or in case of diffusion steps limited by nearest neighbors. To the best of our knowledge there is no report about computer simulation researches which takes into account several adsorption site types on different NP faces and possible spillover effect.

We performed simulations for different values of external chemical potential and adsorption energy of CO on support and measured equilibrium coverage of simulated NP. On the addressed range of CO-support adsorption energy (from -2,04 eV to -1,5 eV) we did not find significant influence of spillover effect on equilibrium NP coverage. We suppose that in a framework of the model this effect can not be revealed, due to stochastic nature of the employed method which is not able to properly consider direction of CO flows between NP, support and external environment. Apparently, introduction of reaction on NP or support surface can reveal diffusion of CO molecules between them and show role of spillover effect in such reactions.

References

[1]. C.G. Vayenas et al, “Promotion, Electrochemical Promotion, and Metal–Support Interactions: The Unifying Role of Spillover” in “Catalysis and Electrocatalysis at Nanoparticle Surfaces”, Marcel Dekker, New York, 2003.

[2]. M. Borowko, “Adsorption on Heterogeneous Surfaces” in “Adsorption Theory, Modeling, and Analysis”, Marcel Dekker, New York, 2001.

[3]. H.-T. Chen, J. Comput. Chem. **2009**, 31, 258–265.

[4]. F. Cleri, V. Rosato, Phys. Rev. B **1993**, 48 22–33.

[5]. H. Orita, N. Itoh, Y. Inada, Chem. Phys. Lett. **2004**, 384, 271–276.

[6]. S. Yamagishi, T. Fujimoto, Y. Inada, H. Orita, J. Phys. Chem. B **2005**, 109, 8899–8908.

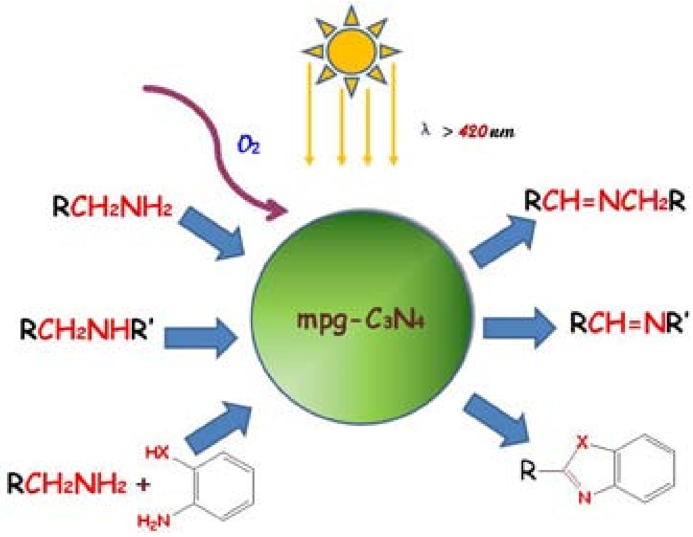
AEROBIC OXIDATIVE COUPLING OF AMINES BY CARBON NITRIDE PHOTOCATALYSIS WITH VISIBLE LIGHT

Fangzheng Su[1], **Smitha C. Mathew**[2], **Siefried Blechert**[2],
Markus Antonietti[1], **Xinchen Wang**[1]

[1]*Department of Colloid Chemistry, Max-Planck Institute of Colloids and Interfaces,*
Research Campus Golm, 14476 Potsdam (Germany),
E-mail: Fangzheng.Su@mpikg.mpg.de
[2]*Institut für Chemie, Technische Universität Berlin, Strasse des 17. Juni 135,*
D-10623 Berlin (Germany)

The utility of cheap, clean and renewable energy source such as the solar energy to induce the chemical reactions serves as a promising way for the cost-effective and green chemical synthesis [1]. Recent years have witnessed the growing interest in photochemical transformations as the activation of substrate may happen without additional reagents under the principle of green chemistry.

Recently, we introduced a simple and potentially abundant polymeric semiconductor, a weakly disordered version of graphitic carbon nitride (g-C_3N_4) as a metal-free photocatalyst for hydrogen evolution with visible light [2]. The light-induced electron with large reduction potential can easily activate molecular oxygen to mediate energy and electron transfer while the moderate oxidation potential of the holes prevents the synthesized organics from deep oxidation in an uncontrollable manner. This feature suggested that g-C_3N_4 can act as a gentle photocatalyst for promoting organic redox synthesis in a broader fashion.



Scheme 1. mpg-C_3N_4-catalyzed Aerobic Oxidative Coupling of Amines.

Herein, we report the aerobic oxidation of a wide range of amines to imines in excellent yields using mesoporous carbon nitride (mpg-C_3N_4) activated by visible light. We also integrate this oxidative coupling scheme to a one-pot synthesis of benzoxazoles, benzimidazoles and benzothiazoles, which are interesting and important compounds that occur widely as biologically active natural products, as well as marketed drugs or drug candidates [3].

References

[1]. N. Hoffmann, Chem. Rev. **2008**, 108, 1052.

[2]. X. C. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, K. Domen, M. Antonietti, Nat. Mater. **2009**, 8, 76.

[3]. Y. Shiraishi, Y. Sugano, S. Tanaka, T. Hirai, Angew. Chem. 2010, 122, 1700; Angew. Chem. Int. Ed. **2010**, 49, 1656.

Acknowledgements

Unicat, 973 Program (2007CB613306), NCET (07-0192), and ENERCHEM project of the Max Planck Society.

MECHANISMS FOR CHEMICAL REACTIVITY OF TWO KINDS OF POLYMER MODIFIED ASPHALTS DURING THERMAL DEGRADATION

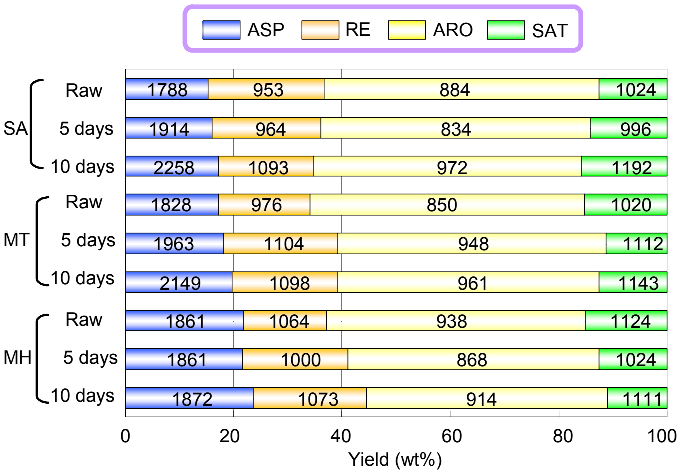
Motoyuki Sugano[1], **Jun Kajita**[1], **Mitsue Ochiai**[1], **Noriyuki Takagi**[1], **Shigeo Iwai**[2], **and Katsumi Hirano**[1]

[1]*Nihon University, Graduate School of Science and Technology,*
Department of Materials and Applied Chemistry,
E-mail: sugano@chem.cst.nihon-u.ac.jp
[2]*Department of Transportation Engineering and Socio-Technology.*

Introduction In Japan, about 85% of polymer modified asphalt (MA) was produced by modification of straight asphalt (SA) with styrene – butadiene – styrene triblock copolymer (SBS). It is well known that MA has superior property as binder in the pavement. In order to design the recycle process and lengthen of life of MA, degradation mechanism of MA must be clarified. Two kinds of MA, such as second type of MA (MT) and H type of MA (MH), are widely used in the pavement. In this study, the variations in the chemical characteristics of MT during thermal degradation process are compared with those of MH.

Experimental The thermal degradation of SA, MT and MH was carried out at 190 °C for 5 and 10 days in nitrogen gas. After each sample was extracted with n-hexane, the n-hexane insoluble (asphaltene; ASP) and soluble (maltene) materials were prepared. After maltene was placed at the top of activated alumna filled in the glass column, n-hexane, toluene, and mixture of methanol and toluene were successively flowed into the glass column. The fractions from these eluates were referred as saturates (SAT), aromatics (ARO) and resins (RE), respectively.

Results and Discussion Yields of four constituents before or after thermal degradation of SA, MT and MH are shown in Fig. 1. With the increase of term of thermal degradation, the yields of ASP in SA, MT and MH increased gradually. However, the SAT yield in SA and the RE yields in MT and MH increased gradually. On the other hand, increased yield of ASP in MH by thermal degradation was smaller than those of SA and MT. With the increase of term of thermal degradation, the increased amount of the average molecular weight of ASP in SA was larger than that in MT. On the other hand, the average molecular weight of ASP in MH was almost constant. The molecular weight distributions (GPC profiles) of SBS before or after thermal degradation of MT and MH are shown in Fig. 2. In comparison with the height ratio of two peaks of raw SBS, those of SBS in both MT and MH increased.



Values in the figure denote the average molecular weight of each constituent.

Fig. 1. Yields of four constituents before or after thermal degradation of SA, MT and MH.

Therefore, it was clarified that decomposition of SBS occurred during preparation of MT and MH. The height ratio of SBS in both MT and MH increased with the increase of term of thermal degradation. The content of radicals (not shown in this abstract for lack of space) in MH was lower than those of SA and MT. Therefore, it is considered that generation of radicals was suppressed by addition of SBS. The contents in SA, MT and MH increased with the increase of term of thermal degradation. However, the increased contents of radicals of MT and MH were lower than that of SA, and the suppressive effect in MH with the increase of term of thermal degradation was stronger than that in MT. Accordingly, with the increase of term of thermal degradation, it is considered that the content does not increase significantly for MH with small content of radicals. It was reported that the asphalt constituents in MT and MH were swelled into SBS molecules due to the incorporation of 9 hold weight of the asphalt constituents (RE, ARO) into the SBS molecule [1]. Therefore, only a part of asphalt constituent was swelled by SBS molecule in MT because SBS content in MT is only 5%. Accordingly, the asphalt constituents outside the SBS molecules in MT formed a continuous phase of straight asphalt. On the other hand, most part of the asphalt constituents in MH was swelled into the SBS molecules owing to the high content (9%) of SBS in MH. Therefore, the SBS molecules in MH formed a continuous phase of SBS. During thermal degradation process of MH, it was estimated that the thermally stable SBS molecules protected the thermally unstable asphalt constituents in MH due to incorporation of the asphalt constituents into the SBS molecules. Therefore, the content of radicals in MH was lower than those of SA and MT. During thermal degradation process of MT, the content of radicals increased because the thermally unstable asphalt constituents (SAT, ARO) outside the SBS molecules decomposed. It was considered that the radicals formed from the thermally unstable asphalt constituents polymerized with the SBS molecules and other asphalt constituents. As a result, both decomposition of the

SBS molecules and increases of polar constituents (ASP, RE) occurred during thermal degradation of MT. Therefore, the increased content of radicals during thermal degradation of MT was higher than that of MH. Accordingly, it was clarified that the continuous phase of straight asphalt and the dispersed SBS molecules decomposed simultaneously during thermal degradation process of MT. During thermal degradation process of MH, the average molecular weight of ASP did not increase. Further, in comparison with the thermal degradation of MT, decomposition of the SBS molecules in MH was not enhanced due to suppression of the increase of radical content in MH. Accordingly, during thermal degradation process of MH, the continuous phase of SBS decomposed, however, the dispersed constituents of straight asphalt did not decompose significantly. During thermal degradation of both MT and MH, it was considered that the decomposed SBS molecules combined with the asphalt constituents, which resulted the increases of RE yields.

Conclusions During thermal degradation of both MT and MH, the decomposed SBS molecules combined with the asphalt constituents, which resulted the increases of RE yields. During thermal degradation process of MH, the content of radicals in MH was lower than that of MT due to incorporation of most of the asphalt constituents into the SBS molecules. As a result, in comparison with MT, decomposition of the SBS molecules and the increases of the yield and the average molecular weight of ASP were suppressed with the increase of term of thermal degradation of MH.

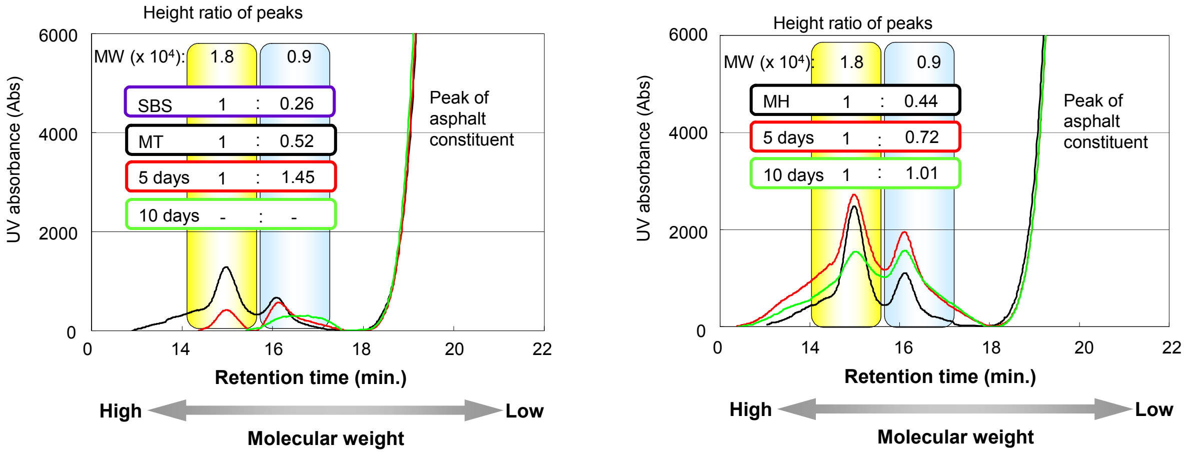


Fig. 2. Molecular weight distributions of SBS before or after thermal degradation of MT (left) and MH (right).

References

[1]. Uesaka, K., et al. Journal of Pavement Engineering, JSCE, **2005**, 10, 213-219.

PP-III-71

BIO-OIL PRODUCTION FROM FAST PYROLYSIS OF KELP IN THE SOUTHERN COAST OF KOREA

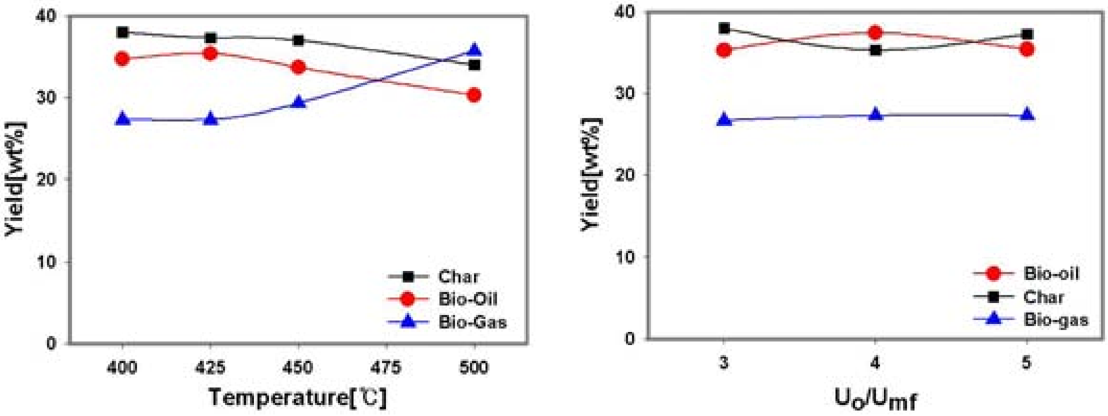
Dong Jin Suh, **Jae-Wook Choi, Young-Woong Suh**

Clean Energy Center, Korea Institute of Science & Technology,
Cheongryang, Seoul 136-791, Korea, djsuh@kist.re.kr

Biomass is recognized as a renewable energy source due to the depletion of fossil fuel reserves. Biomass is biological material derived from living, or recently living organisms including organic wastes. Biomass can be converted to more useable forms of energy by biological, thermochemical and physical methods. Of the thermochemical methods, pyrolysis has received great attention since it can produce a liquid product, termed bio-oil or pyrolysis oil, which has an advantage in storage and transport. Fast pyrolysis is a thermal degradation of organics in the absence of an oxidizing agent, and can produce gas, liquid and solid products [1]. The yields and properties of the liquid product depend on the feedstock, the reactor type and the process conditions [1,2]. In terms of biomass feedstock, research interests have been focused on the lignocellulosic biomass such as woods, plants and argicultural residues. Few studies have been reported the conversion of macroalgae by pyrolysis [3,4]. In this work, kelp in the southern coast of Korea, was investigated. Pyrolysis experiments were carried out under different conditions in a bubbling fluidized bed reactor. The influence of pyrolysis temperature and the ratio of nitrogen velocity to minimum fluidizing velocity on the product yields was investigated. The chemical composition of the pyrolytic oil was analysed by GC/MS system.

Figure 1 (a) showed the influence of pyrolysis temperature on the product yields. As the pyrolysis temperature was increased, bio-oil yield increased up to 36 % and then gradually decreased at above 425°C whereas bio-gas yield drastically increased to a maximum of 35 % at 500 °C. These results indicated that the pyrolysis vapors was converted to gas products through their secondary cracking at higher pyrolysis temperatures. The bio-oil yield of Kelp was lower than that of lignocellulosic biomass [5] because it contained a lower amount of volatile fraction. Char yield also decreased as the pyrolysis temperature was raised from 400°C to 500°C. Experiments were conducted to find the optimum ratio of nitrogen velocity (U_0) to minimum fluidizing velocity (U_{mf}) at a fixed pyrolysis temperature of 425°C. The sweeping gas during pyrolysis could affect the residence time of the pyrolysis vapor and as a resut, could enhance bio-oil yield by minimizing secondary reactions such as thermal cracking, repolymerisation and recondensation. The effect of U_0/U_{mf} ratio on the product yields was shown in Figure 1 (b). The highest bio-oil yield of 36% was achieved with U_0/U_{mf} ratio of 4 and there was no obvious influence on the yield of gas and char as U_0/U_{mf} ratio was increased. Therefore, the optimum pyrolysis temperature and U_0/U_{mf} ratio for achieving maximum bio-oil yield were 425°C and 4, respectively. The qualitative and quantitative analysis of bio-oil was conducted by GC/MS system. About 30 peaks were identified by GC/MS software library. The main compounds were classified by aliphatics, phenolics, furans, cyclopentane and then each fraction was calculated from peak area. The most abundant group of bio-oil was aliphatics and this differs significantly from the bio-oil composition obtained from lignocellulosic biomass [5].

From the above results, it is believed that the utilization of kelp for producing useful chemicals or fuels by fast pyrolysis seems to be promising although it is dependent upon availability of resources.



(a) Influence of pyrolysis temperature

(b) Influence of U_0/U_{mf} ratio

Figure 1. The influenc of experimental conditions on the product yields.

References

[1]. A. V. Bridgewater, *J. Anal. Appl. Pyrol.* 51 **(1999)** 3.
[2]. D. Meier and O. Faix, *Biores. Technol.* 68 **(1999)** 71.
[3]. X. Miao et al., *J. Anal. Appl. Pyrolysis* 71 **(2004)** 855.
[4]. T. Minowa et al., *Fuel* 73 **(1994)** 1855.
[5]. Q. Zhang et al., *Energy Conversion & Management* 48 **(2007)** 87.

Acknowledgements

The authors would like to acknowledge funding from the Korea Institute of Science & Technology and the Korean Ministry for Food, Agriculture, Forestry and Fisheries.

PP-III-72

HORSERADISH PEROXIDASE IMMOBILIZATION IN CATALYTIC OXIDATION OF PHENOLS

Sulman M., Sidorov A., Lakina N., Sulman E., Tikchonov B., Matveeva V., Doluda V.

Dept. of Biotechnology and Chemistry, Tver Technical University, A. Nikitin str., 22, Tver, 170026 (Russia) sulman@online.tver.ru

The use of the immobilized enzymes in modern industrial catalysis is in great demand. These are the major reasons for attaching enzymes to various supports: (i) multiple or repetitive use of a single batch of enzymes; (ii) the ability to stop the reaction rapidly by removing the enzyme from the reaction solution; (iii) enzymes are usually stabilized by binding; (iv) product is not contaminated with the enzyme; (v) analytical purposes - long 1/2-life, predictable decay rates, elimination of reagent preparation. The surface on which the enzyme is immobilized is responsible for retaining the structure in the enzyme through hydrogen bonding or the formation of electron transition complexes. These links will prevent vibration of the enzyme and thus increase thermal stability. The microenvironment of the surface and the enzyme has a charged nature that can cause a shift in the optimum pH of the enzyme of up to 2 pH units. Thus, while developing reusable catalytic systems on the basis of immobilized enzymes one of the main problems is the choice of the firm carrier for the immobilization of enzyme which will provide its best stabilization. The application of traditional (alumina, silica, ion-exchange resins) and polymer-modified supports is an effective solution to this problem.

In this study the catalytic systems on the base of immobilized horseradish peroxidase (HRP) were successfully applied in the reaction of phenol oxidation in the presence of hydrogen peroxide. Various catalytic systems were synthesized: (i) HRP immobilized on alumina modified with polyelectrolytes (chitosan (CS) and poly(sodium 4-styrenesulfonate)), (ii) HRP immobilized on CS-modified cation-exchange and anion-exchange resins. Carbodiimide (CD) and glutaric aldehyde were used as linking agents.The extraction of HRP was carried out from disintegrated fresh root of horseradish. The activity of the obtained catalyst on the base of ion exchange resins remains practically constant at the repeated application in the reaction of phenol oxidation. Among the catalysts on the base of ion-exchange resins CS-modified cation-exchanger was the most effective one (99.5 % of phenol conversion). Al_2O_3/PSS/CS/CD/HRP catalyst revealed 99% of phenol conversion. Thus the catalytic systems obtained can be used for sewage and industrial waste biocatalytic treatment from dangerous phenolic compounds by their oxidation up to less dangerous biopolymers.

Acknowledgements

We sincerely thank NATO science for peace programme Sfp 981438 for the financial support.

PP-III-73

PHOTOCATALYTIC DEGRADATION OF DYE POLLUTANT OVER Ti AND Co DOPED SBA 15: COMPARISON OF ACTIVITIES UNDER VISIBLE LIGHT

Suraja P.V.[1], Yaakob Z.[1], Binitha N.N.[1,2], Silija P.P.[1]

[1]*Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment, National University of Malaysia, 43600 UKM Bangi, Selangor, Malaysia, Ph: +60 (3) 8921 6400. Fax: +60 (3) 8921 6148,*
E-mail: binithann@yahoo.co.in, zahira@eng.ukm.my
[2]*Department of Chemistry, Sree Neelakanta Government Sanskrit College Pattambi, Palakkad-679306, Kerala, India*

Cobalt and titanium loaded thick-wall hexagonally ordered SBA-15 mesoporous material catalysts are prepared by impregnating the metal precursor solution on the hydrothermally stable support. Their properties are compared using various techniques. Nature of Co and Ti over SBA is investigated using FTIR spectra and XRD analysis. XRD shows the existence Co as its spinel structure Co_3O_4 and Ti as its anatase TiO_2 phase. FTIR shows (Fig. 1) the absorption bands of Co_3O_4 at around 667 and 565 cm^{-1}. UV-VIS DRS analysis gives an idea about the visible light absorbance of the systems. The surface area is investigated using BET method and change in surface area after doping is a result of the insertion of the metal. Both type of systems are found to be promising photocatalysts for pollutant degradation under visible light. Co_3O_4 and anatase TiO_2 is already proved photocatalysts and here SBA 15 support leads easy separation of the catalysts from the cleaned solution. In the case of cobalt loaded SBA 15, activity is found to be maximum at a cobalt loading of 40% whereas 50% Ti containing SBA 15 is found to be most active among the prepared systems for the degradation of the dye pollutant methylene blue (Fig. 2).

Acknowledgements: The authors acknowledge the UKM, the grant number UKM-OUP-NBT-27-118/2009 for the financial support.

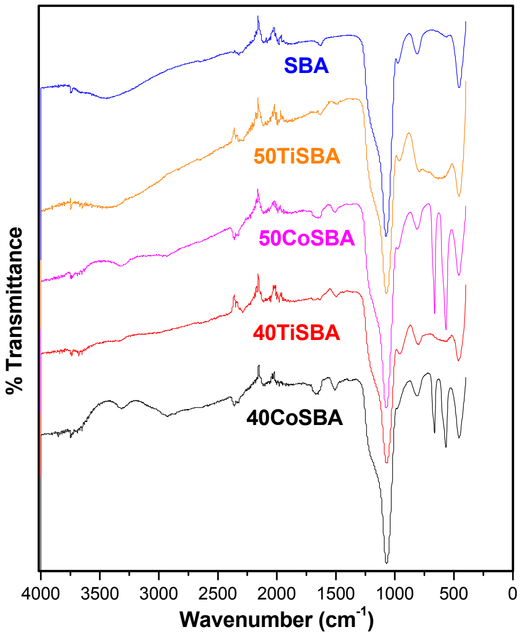


Figure 1. FTIR of SBA 15 systems with different percentage metal loading.

Figure 2. Degraded methylene blue solution under visible light using different catalysts.

PP-III-74

USE OF NATURAL GAS CONVERSION FOR POWER EFFECTIVENESS INCREASE OF BLAST-FURNACE PRODUCTION

Tomash M.A., Sushchenko A.V.

MSc, PSTU, E-mail: syncma@mvs.net.ua
Ph.D, associate professor PSTU, E-mail: sushchenko_a_v@pstu.edu

Blast-furnace process remains the most economical in comparison with other known ways of iron reduction melting. The heat consumption for 1 ton of pig iron in blast furnace is 25 – 80 % lower than in cokeless processes of pig-iron melting, such as "Corex" and "Romelt".

One of the most important indicators of energy efficiency at the metallurgical works is metallurgical coke consumption in blast furnaces. At the best steel companies in the world (Japan, China and others), the coke consumption is 260 - 280 kg per ton of pig iron. In the European countries the average rate of coke consumption is 350 - 360 kg per ton of pig iron [1]. Ukraine lags behind significantly; the best up-to-date figure is 420 - 440 kg per ton of pig iron. At the majority of Ukrainian metallurgical works the average rate of coke consumption is 490 - 510 kg per ton of pig iron. And consequently, the development of measures for reduction of power inputs in blast-furnace production is one of the most important tasks of the domestic steel industry.

One of the effective ways to reduce the consumption reduction of thermal energy to the pig-iron melting in a blast-furnace is use of top gas chemical energy in blast-furnace process. We suggest using the blast furnace gas for natural gas conversion and obtaining a reducing gas. It is shown that of all types of natural gas conversion: steam, oxygen, carbon dioxide, steam conversion is the most effective for the conditions of the blast furnace. The advantage of this method is the large volume of this reducing gas, the shortcoming of this method is the need for additional heat for the reaction. For steam conversion of natural gas it is better to use continuously working converter which avoids contact of sulfur compounds with nickel catalyst.

We suggest a technological scheme of the blast furnace with enter of pulverized coal feed (PCF) into the furnace and hot reducing gases (HRG) to the bottom of the blast furnace stack. After leaving the blast furnace top gas passes normal three-step purification and enters the collector. Part of the top gas is taken away for nozzle stove heating. Another part of the blast-furnace gas enters the gas network of the metallurgical works, and is used as a gas fuel by other workshops. About 50% of blast furnace gas enters the converter, burns in it supporting the temperature of 1050 – 1100 °C inside the converter. Smoke fumes which are formed, leave the converter and pass through the recuperator and release into the smokestack. Mixture of steam and natural gas heated to 400 °C passes through the recuperator and enters the gas pipe of reformer, filled with catalyst, where steam conversion runs. Converted gas enters the upper row of the blast furnace lances at the bottom of the blast furnace stack. Hot blast with the temperature of 1250 °C and pulverized coal enter the blast-furnace hearth through the lower lances.

The proposed technology of blast-furnace melting is based on the concept of autonomy of the upper and lower zone of a blast furnace. Pulverized coal feed (PCF) injected into the blast-furnace hearth reduces the lack of heat in the hearth and coke specific consumption due to its direct replacement of coal dust. Hot reducing gases supplied into the blast furnace stack eliminate the lack of reducing gases in this section and bring down the coke specific consumption due to more complete reduction of iron oxides by gases and descent of the direct iron reduction. If hot reducing gas consumption is sufficient the degree of direct iron reduction must be closely approximated to 0 and the run of blast furnace melting – to the ideal process of Gryunerovsky [2] without any additional solid fuel consumption in the blast-furnace hearth at high technological parameters of the process. Steam conversion of natural gas improves the efficiency of its use in blast-furnace melting 1.5 times as much. Replacement ratio of blast-furnace coke by natural gas increases from 0.7 to 1.0 – 1.05 kg / m^3 by expanding the amount of the reducing gases in comparison with the traditional blowing of natural gas into the blast-furnace hearth. The use of secondary energy resources such as blast furnace gas for steam conversion improves the efficiency of natural gas with minimal consumption.

References

[1]. Производство первичного металла в странах западной Европы / Бабич А.И., Кочура В.В., Формосо А., Гарсия Л. // Металл и литьё Украины. - **1997.** - № 5. - С. 32 – 37.

[2]. Ефименко Г.Г. Металлургия чугуна // Г.Г. Ефименко, А.А. Гиммельфарб, В.Е. Левченко. – К.: Высшая школа, **1988**. – 351 с.

THERMOCATALYTIC DEGRADATION OF POLYSTYRENE AS AN EFFICIENT METHOD FOR NEUTRALIZATION OF PLASTIC WASTES

Karina Tomaszewska, Joanna Kałużna-Czaplińska, Wojciech Jóźwiak

Institute of General and Ecological Chemistry Technical University of Lodz,
ul. Żeromskiego 116, 90-924 Łódź, e-mail: karinatom@poczta.onet.pl

Polystyrene (PS) is one of the most popular materials for producing packaging, household goods, toys, etc. Unfortunately, the increase in the use of plastics has resulted in a growth of waste production. In spite of the fact that we live in the 21st century, the most common solution to this problem is still dumping waste at landfill sites. It's due to low level of rubbish segregation (especially in developing countries) and high dispersion of used plastics amongst other waste products. Large volume of polymers together with a relatively low weight expand the transport costs and cause rapid overfilling of the landfills. One of the efficient methods using for neutralization of polystyrene wastes is production of fuels in thermal cracking processes, in which the plastics recovered from waste are thermally or thermo-catalytically degraded into valuable oils [1, 2].

In the present work, we have investigated the influence of the montmorillonite type (mK5, mK10, mK20, mK30) and zeolite Y type (Y_{Na^+}, $Y_{NH_4^+}$) catalysts on the degradation of polystyrene to fuel oils process. Thermal analyses TG-DTA-MS were carried out in an argon flow with the use of a Setaram thermobalance unit (Setsys 16/18) connected to the Balzers quadrupole mass spectrometer (Thermostar). To determine the activation energy of thermal and thermo-catalytic degradation of PS processes Arrhenius equation was used [3–5]. The activity tests were carried out in an in-house designed stainless steel reactor by batch operation under the atmospheric pressure. The reaction products were classified into three groups: gases, liquids and solid residues. The desired products — liquids were studied during the GC-MS analyses. The examinations were carried out on an Agilent Technologies 6890N Network GC coupled to 5973 Network Mass Selective Detector.

Isothermal TG-DTA-MS analyses of PS degradation were carried out at a constant temperature ranged from 380 to 480 °C, both for thermal and catalytic processes to determine the effect of temperature and used catalyst on the reaction time and activation energy. The results of thermal PS degradation at different temperatures are presented in Fig. 1.

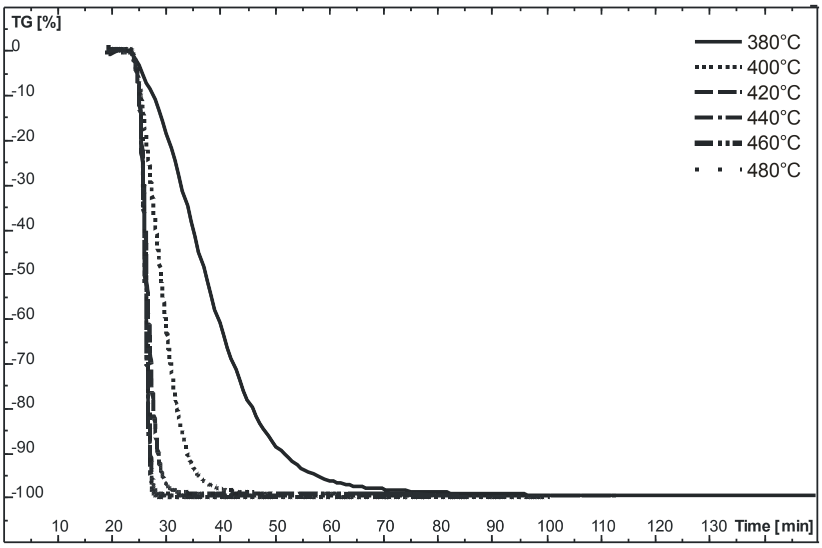


Figure 1. TGA curves of the polymer mass loss during thermal degradation of PS at different temperatures.

One can observe that time necessary to complete the degradation of PS in isothermal process is related to the process temperature. At the lowest temperature (380°C) the degradation process takes over 95 minutes while at 480°C only 9 minutes. The estimated activation energy for this process was about 90 $kJ \cdot mol^{-1}$. There is also a clear difference between the time of thermal and catalytic degradation — non catalytic process goes on several times longer than catalytic one (the time of the reaction depends on the kind of used catalyst). The degradation of PS was studied also in dynamic conditions with different heating rates to determine the influence of a heating rate for given catalyst on the reaction temperature.

GC-MS analyses of liquid products were carried out to define the influence of applied catalyst on the hydrocarbons mixture composition. In the thermal degradation of PS, many aromatic hydrocarbons with a wide-range distribution of carbon atom numbers are formed. In contrast, the oils produced in the catalytic degradation process are known to contain a narrower distribution of hydrocarbons.

References

[1]. Mucha M.: Polimery a ekologia, Wydawnictwo Politechniki Łódzkiej, Łódź 2002.
[2]. Stelmachowski M.: Termokatalityczna degradacja polimerów, Polska Akademia Nauk, Łódź 2003.
[3]. Pielichowski K., Njugana J.: Thermal degradation of polymeric materials, Rapra Technology Limited, Shawbury 2005.
[4]. Reverte C., Dirion J.L., Cabassud M.: J. Anal. Appl. Pyrolysis **2007**, 79, 297–305.
[5]. Abate L., Blanco I., Pollicino A., Recca A.: J. Therm. Anal. Calorim. **2002** 70, 63–73.

Acknowledgements

Authors acknowledge financial support of the Ministry of Science and Higher Education (Grant no. N205 025 32/1352).

PP-III-76

TECHNOLOGICAL ASPECTS OF WASTE WATER TREATMENT FROM ORGANIC POLLUTANTS

Torosyan G.[1], Isakov A.[1], Kudryavtsev A.[1], Harutyunyan S.[2], Hovhannisyan D.[3]

[1]State Engineering University of Armenia, department of chemical technology & environmental engineering, Yerevan, Armenia, e-mail: gagiktorosyan@seua.am
[2]Yerevan State Economic University Yerevan, Armenia
[3]Yerevan university of Architecture & Construction, Yerevan, Armenia

It has been investigated an adsorbtive abilities of sorbents available in Republic Armenia, in particular H-mordenit and the activated coal made of plum stones, in relation to organic pollutants for the purpose of device-technological design of process of waste water treatment. As organic pollutants here was studied the most known water pollutants as aniline, phenol, toluene and malathion.

Here are offered cross-step or counter-flow schemes For waste water treatment process device design. At equal number of the basic devices in the considered schemes preference it is given counter - step scheme.

The researches were spent in static conditions on a laboratory rocking chair. Sorbents in quantity of 1,0 ±0.01 g brought in water solutions, volume 100 ±0.1 ml containing organic compounds in quantity from the maximum solubility to maximum concentration limit for each substance. Further a mix placed on a rocking chair and subjected to hashing during during 6h., at temperature of 20° , then test defended within 24 h. Residual quantities of substances were defined by methods of UV-spectroscopy and HLECh (system Water 486-detector, Water 600S - controller, Water 626-Pump, a column 250x4 mm filled microspherical silica as sorbent, speed of a stream of a mobile phase of 1 ml/mines).

On the basis of the analysis of data isotherms of adsorption which have been processed by means equations of Dubinin-Radushkevich, Langmuir, Friendlich have been constructed [1].

On the basis of the received experimental and settlement data mathematical models of the technological scheme of adsorbtive water treating from noted pollutants have been deduced. On superficial groups of hydro group and atoms of oxygen of H-zeolites processes of formation of chemical bonds owing to molecular interactions with groups of hydroxyl / for phenol/ and amino groups / for aniline / proceed.

The elementary version of device-technological design of adsorbtive waste water purifications is use of the block from two devices – the blender in which sorbent suspension in cleared water mixes up before achievement adsorbtive balance, and sediment bowl in which fulfilled adsorbent separates from the cleared water. Calculation of such scheme, taking into account the maximum adsorption data of pollution from water environments the specified sorbents, has shown that the expense of the last is inadmissible is great (for example, in the case of phenol it will make 1,745 kg/l for H - mordenite, and for the activated coal made of plum stones – 2.54 kg/l, at initial concentration 1 g/l) [2,3]. Considerably to reduce the expense of adsorbent use of more perfect schemes of device design – crossing-step or counter-flow allows.

As in both considered schemes at equal number of the basic devices and, hence, identical capital investments when economic feasibility is defined by operational expenses, preference, certainly, it is necessary to give counter flow-step scheme.

References

[1]. Koganovsky A.M., Klimenko N.A., Levchenko T.M., Roda I.G. (1990). - Adsorption of organic substances from water, Leningrad Chimia, p. 256

[2]. Torosyan G.H., Aleksanyan A.R., Martirosyan V.G., Galstyan G.F., Davtyan V.A.,.Sarkizova J.S., Kazinyan A.A. (2008), Use agricultural residues as a sorbent for removal of organic substances from water solutions, Chemistry and Chemical Technology (Russia). **51**, 12, 99-101.

[3]. Torosyan G.H., Isakov A.A., Hohannisyan D.N. (2006) The sorbent for thin sewage treatment from organic pollutants // Bulletin of International Ecological association, Sankt Petersburg. **11**, N8, 2. 58-61.

Acknowledgment

This work was supported by the grant from Ministry of Higher education & Science of Republic of Armenia. We gratefully acknowledge to Engineer Anatoly Isakov for their kind help and comments.

INFLUENCE OF DIFFERENT METALLIC AND ACID FUNCTIONS ON DIMETHYL ETHER STEAM REFORMING

Vicente J., **Remiro A., Valle B., Ereña J., Gayubo A.G.**

Chemical Engineering Department. University of the Basque Country.
P.O. Box 644, 48080 Bilbao, Spain.
Tel: 34-94-6015361: Fax: 34-94-6013500: e-mail: jorge.vicente@ehu.es

Introduction. Dimethyl ether steam reforming (DME SR) is currently regarded as a promising process for H_2 production for both present industries and new technologies for fuel cells [1]. DME SR comprises two moderately endothermic reactions in series: 1) DME hydrolysis to methanol (MeOH) on an acid function, such as γ-Al_2O_3 [2] or zeolites [3]; and 2) MeOH SR on a metallic function, usually based on Cu [4].

This paper studies the influence of different Cu-based functions and acid functions on the activity and stability of bifunctional catalysts in the DME SR. The metallic/acid ratio for maximizing H_2 yield has also been determined.

Experimental. The catalysts have been prepared by a wet mixture of the metallic and acid functions. Three Cu-based metal functions have been prepared by co-precipitation, with Cu/Zn/Al atomic ratios of 2/1/0, 1/1/0, 1/1/0.22 A commercial catalyst (G66) for methanol steam reforming (Cu/Zn/Al = 2.75/1/0.42) has also been used for comparison. A commercial γ-Al_2O_3, a commercial HZSM-5 zeolite (SiO_2/Al_2O_3 = 30, denoted Z30) and a HZSM-5 zeolite modified by alkaline treatment (denoted ATZ30) [5] have been used as acid functions. The metallic and acid functions have been calcined at 325 and 550 °C, respectively. The properties of the catalysts have been studied by ICP, N_2 adsorption, NH_3 differential adsorption and TPD, FTIR, TPR and NO_2 chemisorption. DME SR has been carried out in automated reaction equipment provided with an isothermal fluidized-bed reactor connected on-line to an Agilent 3000 MicroGC. The operating conditions are: space time up to 0.6 $g_{catalyst}h/g_{DME}$, steam/DME/He ratio = 3/1/0.85 and temperature range = 250-400 °C.

Results and discussion. Table 1 shows the values of DME conversion and H_2 yield at 20 minutes of time-on-stream for the bifunctional catalysts studied. The catalysts based on HZSM-5 zeolite allow obtaining the same conversion as the catalyst based on γ-Al_2O_3 but at a considerably lower temperature, due to their acid properties that promote DME hydrolysis to methanol. Consequently, H_2 selectivity and stability of the catalysts are notably improved since the WGS reaction is thermodynamically enhanced (minimizing CO formation) and there is almost no sintering of the metallic function. However, hydrocarbon formation from MeOH and DME takes place above 300 °C on zeolite-based catalysts, which causes a drop in DME conversion and H_2 yield. An induction period is needed for hydrocarbon formation on HZSM-5 zeolite-based catalysts, and the duration of this period significantly decreases with temperature and with the acid strength of the zeolite. Therefore, the catalyst prepared with a zeolite modified by alkaline treatment (which moderates its acidity) is more stable for hydrogen production in a long reaction.

The catalysts with Cu/Zn ratio = 1/1 have higher activity for H_2 production due to their higher metallic dispersion. Moreover, the addition of Al improves the physical properties of the catalyst leading to a better performance at low temperature, but it also enhances hydrocarbon formation above 300 °C. Consequently, the CZA/ATZ30 bifunctional catalyst is suitable for obtaining high DME conversion (> 0.90) in DME SR below 300 °C. This temperature is sufficiently low for minimizing both by-product formation and catalyst deactivation by Cu sintering, which allows attaining high and stable H_2 selectivities (> 96%) and yields (> 90%).

Table 1. DME conversion (X_{DME}) and H_2 yield (Y_{H2}) in the DME SR on different bifunctional catalysts at 20 minutes of time-on-stream. Reaction conditions: 250-400 °C range, water/DME molar ratio = 3/1 and space time of a) 0.595 $g_{catalyst}$·h/g_{DME} and b) 0.298 $g_{catalyst}$·h/g_{DME}.

	X_{DME}				Y_{H2}			
T (°C)	275	300	325	400	275	300	325	400
G66/γ-Al_2O_3[a]	-	0.06	0.25	0.87	-	0.06	0.23	0.81
G66/Z30[a]	0.79	0.88	0.86	-	0.76	0.85	0.52	-
G66/ATZ30[a]	0.69	0.84	0.91	-	0.61	0.78	0.83	-
G66/ATZ30[b]	0.40	0.56	0.62	-	0.35	0.48	0.47	-
CZ(2:1)/ATZ30[b]	0.37	0.50	0.65	-	0.31	0.43	0.60	-
CZ(1:1)/ATZ30[b]	0.62	0.75	0.83	-	0.55	0.73	0.81	-
CZA/ATZ30[b]	0.66	0.79	0.86	-	0.58	0.74	0.76	-

References

[1]. Q. Zhang, F. Du, X. He, Z. T. Liu, Z. W. Liu, Y. Zhou, *Catal. Today*, **2009**, 146, 50.

[2]. D. Feng, Y. Zuo, D. Wang, J. Wang, *Chin. J. Catal.*, **2009**, 30, 223.

[3]. T.A. Semelsberger, K.C. Ott, R.L. Borup, H.L. Greene, *Appl. Catal. A*, **2006**, 09, 210-223.

[4]. K. Cheekatamarla, C. M. Finnerty, *J. Power Sources*, **2006,** 160, 490

[5]. A. Alonso, B. Valle, A. Atutxa, A. Gayubo, A. Aguayo, *Int. J. Chem. Reac. Eng.*, **2007**, 5, Article A61.

Acknowledgements

This work was carried out with the financial support of the Ministry of Science and Technology of the Spanish Government (Project PPQ2006-12006).

COMMERCIAL PROCESS FOR INCINERATION OF VOC IN WASTE GASES ON THE BASE FIBER-GLASS CATALYST

Zagoruiko A.N.[1], **Balzhinimaev B.S.**[1], **Lopatin S.A.**[1], **Balashov V.A.**[1],
Arendarskii D.A.[1], **Gilmutdinov N.R.**[2], **Pogrebtsov V.P.**[2],
Nazmieva I.F.[2], **Sibagatullin G.G.**[2]

[1]Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia;
E-mail: zagor@catalysis.ru
[2]Nizhnekamskneftekhim Company, Nizhnekamsk, Russia

The glass-fiber catalysts (GFCs) reveal unique catalytic performance in many oxidation reactions due to the ability of the glass fibers to stabilize the highly-dispersed nanoclusters of transient metals in the glass bulk [1]-[5]. This results in high catalytic activity and high catalyst resistance to poisoning and deactivation in aggressive reaction media. Notably, excellent catalyst performance is achieved at very low noble metal content (0.01-0.02% wt.) thus providing quite reasonable pricing for the catalyst. The unique catalytic properties of GFCs in many oxidation reactions provide their high attractiveness for application in various environmental processes, mostly connected with abatement of toxic and harmful compounds in industrial waste gases and automotive exhausts.

Earlier the Pt-based GFCs have been identified as an extremely efficient catalyst for deep oxidation of volatile organic compounds in waste gases [6], demonstrating much higher activity than conventional mixed CuCrAl oxide catalyst and higher activity than conventional Pt/Al_2O_3 catalyst despite the fact that the last one contains 20-30 times more platinum.

The GFC-based process of catalytic incineration of VOCs (mostly isoprene, isobutylene and CO) in the waste gases of synthetic rubber production facilities was successfully commercialized at Nizhnekamskneftekhim Company site (Nizhnekamsk, Russia) in 2008. The industrial reactor with waste gas loading up to 15000 st.m^3/hour was charged with 1 tonne of GFC, structured in a form of vertical spiral cartridges [7].

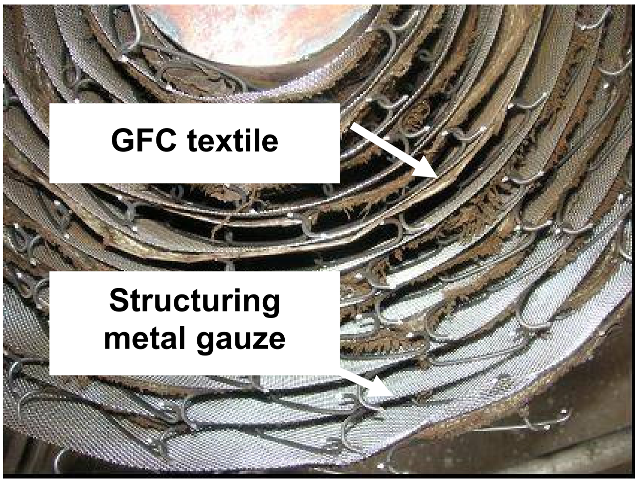


Fig. 1. VOC combustion reactor at Nizhnekamskneftekhim plant (left) and view of the GFC catalyst cartridge (right).

Though the operation conditions were quite complicated (the waste gases have decreased oxygen content as low as 2-3 % vol., the water vapor content was reaching 80% vol. and the gas flow was contaminated with dust particles) the application of GFC leads to increase of abatement efficiency from maximum 70-80% observed earlier for conventional oxide catalyst up to 99.5-99.9%. Catalyst continuous operation for more than 20 months now has revealed no any decrease of catalyst activity, thus giving the ground for quite optimistic estimation of possible GFC lifetime.

References

[1]. L.G.Simonova, V.V.Barelko, O.B.Lapina, E.A.Paukshtis, V.V.Terskikh, V.I.Zaikovskii, B.S.Bal'zhinimaev. *Kinet. Catal.* 42 (2001) 693-702.

[2]. L.G.Simonova, V.V.Barelko, A.V.Toktarev, V.I.Zaikovskii, V.I.Bukhtiarov, V.V.Kaichev, B.S.Balzhinimaev. *Kinet. Catal.* 42(2001) 837-846.

[3]. B.S.Bal'zhinimaev, V.V.Barelko, A.P.Suknev, E.A.Paukshtis, L.G.Simonova, V.B.Goncharov, V.L.Kirillov, A.V.Toktarev, *Kinet. Catal.* 43 (2002) 542-549.

[4]. B.S.Balzhinimaev, L.G.Simonova, V.V.Barelko, A.V.Toktarev, V.I.Zaikovskii, V.A.Chumachenko. *Chem. Eng. J.* 91(2003) 175-179.

[5]. D.A.Arendarskii, A.N.Zagoruiko, B.S.Balzhinimaev. *Chem.Sustain.Dev.* 6(2005) 731-735.

[6]. B.S.Balzhinimaev, E.A.Paukshtis, S.V.Vanag, A.P.Suknev, A.N.Zagoruiko. *Catal.Today*, 2010, in press.

[7]. Russian Patent # 66975, 2007.

Acknowledgements

Authors express their gratitude to the Russian Ministry for Science and Education (State Contract #02.523.12.3005) for the financial support of the research.

LOW TEMPERATURE NH_3-SCR OF NO OVER SUBSTITUTED $MnCr_2O_4$ SPINEL-OXIDE CATALYSTS

Miguel Zamudio, Nunzio Russo, Debora Fino

Department of Materials Science and Chemical Engineering, Politecnico di Torino
Corso Duca degli Abruzzi 24, 10129 Torino, miguel.zamudio@polito.it

Nowadays the most common technique to remove the nitrogen oxides, NO and NO_2 (NO_x) from the exhaust gas in stationary systems is the Selective Catalytic Reduction (SCR) by ammonia. The catalyst V_2O_5-WO_3 (MoO_3)/TiO_2 is one of the most studied and widely commercialized and operates in the temperature range of 300-400°C [1]. Recent studies shows that Mn-based catalysts have good catalytic activity for low temperature NO_x reduction with NH_3.[2-4].

In the present paper, the activity of the stoichiometric and several substituted $Mn_{(1-x)}M_{(x)}Cr_2O_4$ (M=Mg, Ca; x=0.05, 0.01) based spinel-oxides were studied. All the catalysts were prepared by means of the Gel-Combustion method starting from nitrates precursors, citric acid (gelling agent) and glicine (fuel) which were dissolved in deionized water. The obtained final solution was stirred at 70°C and concentrated by evaporation until the gel was formed, then put into the oven at 800°C for 1h and finally calcined at 800°C in air for 2 h. The catalysts were fully characterized by XRD, BET, FESEM, and H_2-TPR analyses in order to assess the cristallinity degree, surface area values, morphology, capability of oxygen desorption and reducibility of the B site.

The catalytic activity of the prepared spinel oxides was performed in a fixed-bed quartz micro reactor by feeding an atmosphere containing 800 ppmv NO, 800 ppmv NH_3, 3% O_2, balanced by He, with a flow rate of 300 ml/min through 0.36 g of catalyst (W/F = 0.08 g·s/cm^3, GHSV ≈ 50,000 h^{-1}). The temperature was increased up to 200°C with an heating rate of 5°C/min. The outlet gas composition was analyzed by means of a Bruker Tensor 27 FT-IR spectrometer.

The XRD spectra showed, for all the synthesized catalysts, diffraction peaks corresponding to the desired catalysts structure; only for $Mn_{0.9}Ca_{0.1}Cr_2O_4$, CaO and Cr_2O_3 peaks were detected. The FESEM micrographs reported in Figure 1evidenced a foamy morphology, with a nanoscopic structure. The specific surface area (SSA) values, reported in Table 1, range between 25 and 50 m^2/g.

All the prepared spinel-oxide catalysts showed high NO conversion rates with a good selectivity to N_2 (higher than 90%). The $Mn_{0,95}Ca_{0,05}Cr_2O_4$, despite the not highest specific surface area, provided the best performance with a 96% of NO conversion at 125°C and a 97% of selectivity to N_2.

Substitutions at the B site increased the reducibility of chromium, as evidenced by the amount of hydrogen consumed during TPR runs and a general increase of the selectivity could be observed. Studies are now in progress to better correlate the catalytic performances with the substitution effects and to evaluate the operative parameters effect (NH_3/NO_x ratio, amount of O_2, GHSV, etc) on the catalytic performance of the best performing catalyst when supported on a ceramic honeycomb.

Table 1. Collection of the results of the catalyst characterization tests concerning the BET specific surface area, catalytic activity and hydrogen temperature programmed reduction.

Catalyst	**BET [m^2/g]**	**Max. NO Conversion %**	**Selectivity to N_2 %**	**Consumed H_2 in TPR run [mmol/g]**
$MnCr_2O_4$	31.9	90 (at 125°C)	91%	3.0
$Mn_{0.9}Mg_{0.1}Cr_2O_4$	41.7	97 (at 150°C)	90%	11.9
$Mn_{0.9}Ca_{0.1}Cr_2O_4$	49.9	84 (at 125°C)	97%	10.2
$Mn_{0.95}Mg_{0.05}Cr_2O_4$	26.9	99 (at 150°C)	93%	4.3
$Mn_{0.95}Ca_{0.05}Cr_2O_4$	36.5	96 (at 125°C)	97%	11.9

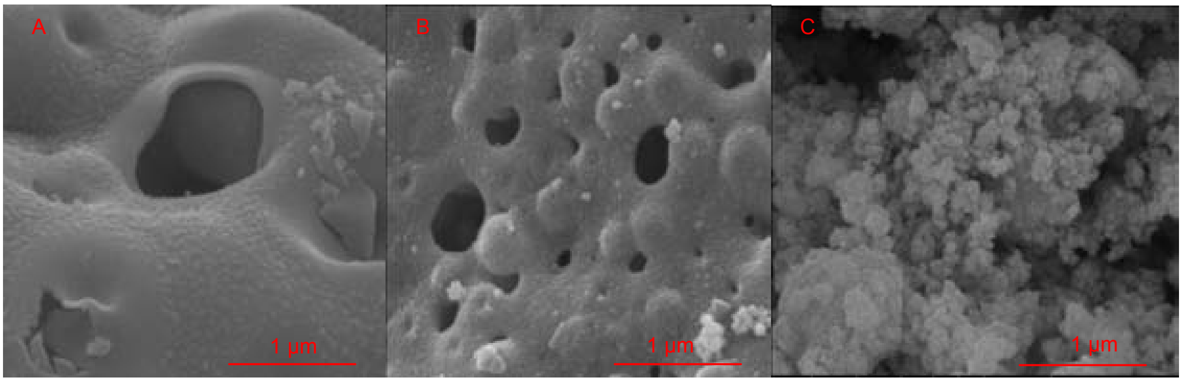


Figure 1. FESEM views of the spinel-oxide catalysts:
A) $Mn_{0.9}Mg_{0.1}Cr_2O_4$; B) $Mn_{0.95}Mg_{0.05}Cr_2O_4$; C) $Mn_{0.95}Ca_{0.05}Cr_2O_4$.

References:

[1]. H. Bosch, F. Janssen, Catalysis Today (1988) 2, 369.
[2]. M. Kang, ED. Park, Kim J M, Yie J E, Applied Catalysis A, (2007) 327(2), 261.
[3]. G. Qi, R. Yang, R. Chang, Applied Catalysis B, (2004) 51, 93.
[4]. Li J, Chen J, Ke R, Luo C, Hao J, Catalysis Communications, (2007), 8(12), 1896.

A NEW PROCESS OF ANTHRAQUINONE PRODUCTION IN THE PRESENCE OF HETEROPOLY ACID SOLUTIONS

<u>Zhizhina E.G.</u>, **Odyakov V.F.**

Boreskov Institute of Catalysis SB RAS,
Prospekt Akad. Lavrentieva, 5, Novosibirsk 630090, Russia;
Fax: 8(383)3 30 80 56, E-mail: zhizh@catalysis.ru

Catalysis by heteropoly (HP) compounds is an intensively developed direction of catalysis especially for processes of fine organic synthesis. The Mo-V-P HP acids (HPA, $H_{3+x}PMo_{12-x}V_xO_{40}$) hold a prominent place among HPA because their reduced forms (H_mHPA) are able to be oxidized with dioxygen [1]. Thus, HPA are *reversibly oxidants*. We have shown that organic compounds of different classes can be oxidized with high selectivity (90-99%) in the presence of the HPA solutions [1].

Catalytic processes of oxidation of any substrates (Su) are combined from two stages (1)+(2) proceeding in different reactors. The target reaction (1) proceeds in ***reactor 1*** at 40-70°C. The catalyst regeneration with O_2 goes in ***reactor 2*** at t > 100°C and O_2 pressure.

$$ {}^{m}/_{2}\,Su + {}^{m}/_{2}\,H_2O + HPA \longrightarrow {}^{m}/_{2}\,SuO + H_mHPA \qquad (1)$$

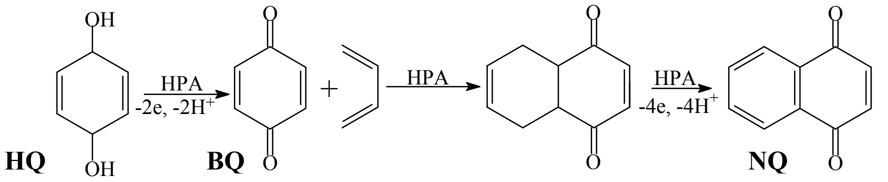
$$ H_mHPA + {}^{m}/_{4}\,O_2 \longrightarrow HPA + {}^{m}/_{2}\,H_2O \qquad (2)$$

The HPA solutions have *bifunctional* (oxidative and acidic) properties. It permits us to use them as bifunctional catalysts in the process of anthraquinone (AQ) production [2].

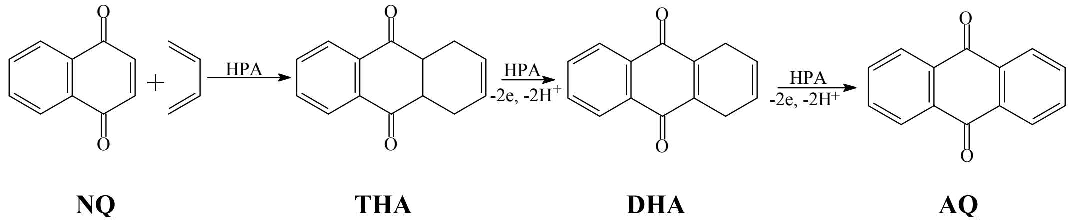
Acylation of benzene by phthalic anhydride according Friedel-Krafts reaction followed by cyclization of *ortho*-benzoylbenzoic acid is the main industrial process of AQ preparation. However, a problem of excessive acid catalysts utilization exists in this process. In another industrial process based on 1,3-butadiene addition to 1,4-naphthoquinone, concentrated alkalies, high boiling organic solvents, and strong inorganic oxidants are used [3]. A growing demand for AQ and its derivatives cannot be supplied with archaic technologies of their manufacture.

We have developed a new one-pot process of AQ production in the presence of the HPA solution in 1,3-butadiene atmosphere [1]. At atmospheric pressure (70-80°C), AQ can be produced from hydroquinone (HQ) by scheme (3)+(4) or 1,4-naphthoquinone (NQ) by scheme (4). In that, we have joined the acid-catalytic reaction of diene synthesis with oxidation of its adducts into one technological stage.

Our new process is pollution-free owing to ability of the HPA solution to repeatedly regeneration with dioxygen.



(3)



(4)

At atmospheric pressure, a mixture of AQ and its partly hydrogenated derivatives, 1,4,4a,9a-tetrahydro-9,10-anthraquinone (THA) and 1,4-dihydro-9,10-anthtaquinone (DHA), is generated in processes (3)+(4). The yield of AQ from NQ in scheme (4) reaches 60%. The yield of AQ from HQ in scheme (3)+(4) is 20%. It is important that reactions (3)+(4) proceed *without organic solvent*. The mixture of slightly soluble AQ+THA+DHA is practically quantitatively separated from the HPA solution by filtration. Studies in Siberian Scientific-Research Institute of Wood and Pull-and-Paper Industry (Bratsk, Russia) have shown that the AQ+THA+DHA mixture is the *effective catalyst for delignification of wood*.

For the solution of the practical problem of production of the delignification catalyst, we have developed new methods of synthesis of thermostable high-vanadium HPA solutions. Their regeneration with dioxygen proceeds very fast in reactor 2 at 160-170°C and ensures high productivity of a whole catalytic process.

References

[1]. *E.G. Zhizhina, V.F. Odyakov, M.V. Simonova.* Kinetika i Kataliz. 2008. V. 49. No. 6. P. 814.
[2]. *E.G. Zhizhina, M.V. Simonova, V.V. Russkikh.* Kataliz v Promyshlennosti. 2005. No. 1. P. 12.
[3]. *V.V. Russkikh.* Khimiya v Interesakh Ustoichivogo Razvitiya. 1999. V. 7. No. 1. P. 85.

PP-III-81

GENERATION OF ELECTRIC ENERGY FROM THE AGRICULTURE WASTE

Maximov A., **Degtev M.**, **Ilarionov S.**

Perm State University, Perm, Russia, htb03_starosta@rambler.ru

The increased requirements to protection of environment against pollution, and the increasing cost of waste processing have revived interest to anaerobic treatment of agriculture waste.

Production of biogas as an intermediate energy carrier is economically justified and it is preferable in processing of constant waste supply, e.g. drains of cattle-breeding and poultry-farming farms, slaughterhouses, vegetative waste, etc. Economic efficiency is connected with absence of the stages of gathering the wastes, and also with constancy of their structure and quantity.

Biogas is produced with the plants of different types and size. This process is especially effective in agriculture where there is a possibility of a full ecological cycle and, for example, sludge remaining after biogas generation is a valuable organic fertilizer [1].

The biogas is obtained as a result of anaerobic digestion of agricultural wastes. It can be used for heating, cooking, etc, but the conversion of biogas into electric one is most interesting from the practical point of view. [2]

Electric can be generated with the help of a gas generator based on an internal combustion engine. This energy can also be generated by using fuel cells of various design.

The developed and tested pilot plant for the generation of electric energy from a liquid and semi fluid waste of livestock farming consists of a preliminary acid fermentation fermenter, a basic methane-tank fermenter, a gas receiver and a gas generator Green Power CC1500. The preliminary acid fermentation fermenter is a 3,0x2,0x0,5 m steel bath; and the basic methane-tank fermenter is 3.2 m^3. A scheme of the biogas pilot plant can be seen in fig.1.

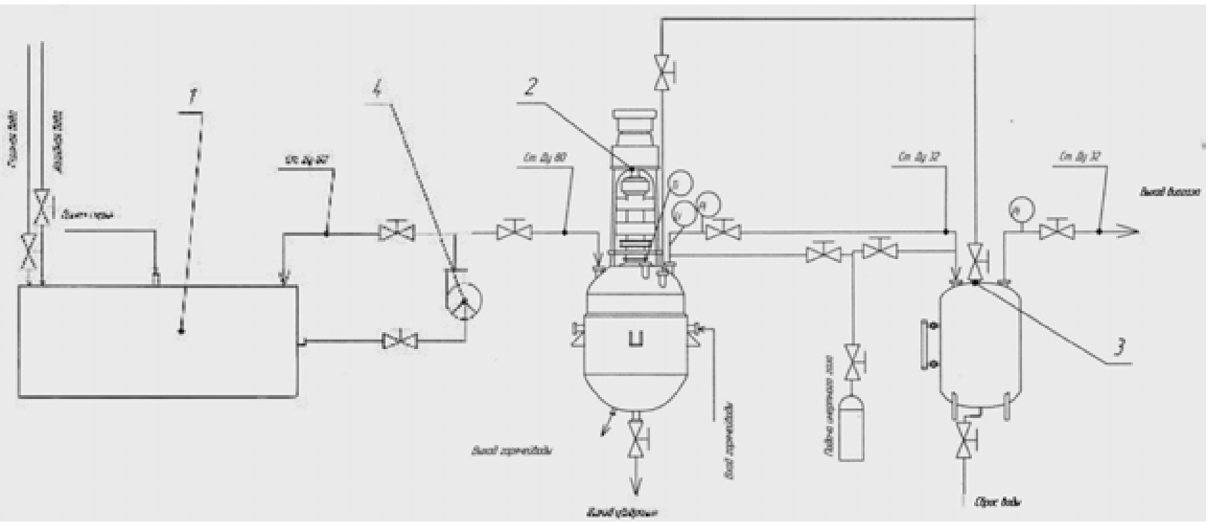


Fig. 1. Scheme of the biogas pilot plan: 1 – a preliminary acid fermentation fermenter, 2 – a basic methane-tank fermenter, 3 – receiver, 4 – a centrifugal pump.

We put 1.4 m^3 of the initial substrate and 0.73 m^3 of water in the preliminary acid fermentation fermenter. After the stage of acid fermentation, the substrate is pumped over into the basic methane-tank fermenter. The process of methane fermentation occurs at temperature 28°C. The time of preliminary acid fermentation is 7 days, the basic methanogenic stage being 30 days.

Chicken dung is used as a substrate. The biogas output is 0.12m^3/h., the content of methane being 60%, carbon dioxide – 38,5%, hydrogen sulphide – 1 %, hydrogen – 1 %. The methane of biogas was detected with a gas Crystal 5000.2 chromatographer. We have used chromatographic column with a zeolite NaX sorbent.

The obtained biogas has been used for the food gas generator Green Power CC1500 with the nominal power output of 1.5 kW and the voltage of 220B.

References

[1]. L.I.Gjunter, L.L.Goldfab. Methantanks. – M: Stroyizdat, 1991. – 128c.
[2]. V.S.Dubrovsky, U.E.Viestur. Metane digestion of agricultural wastes. – Riga: Zinatie, 1988, 204c.

PP-III-82

REACTOR FOR CO OXIDATION EXPERIMENTS ON HETEROGENAZED CATALYSTS ON THE BASIS OF FIBROUS CARBON MATERIALS

Khaminets S.G., Radkevich V.Z., Potapova L.L., Senko T.L., Yegiazarov Y.G.

Institute of Physical-Organic Chemistry of the National Academy of Sciences of Belarus, 13, Surganov St., Minsk 220072, Belarus
E-mail: yegiazarov@ifoch.bas-net.by
radkevich_vz@ifoch.bas-net.by

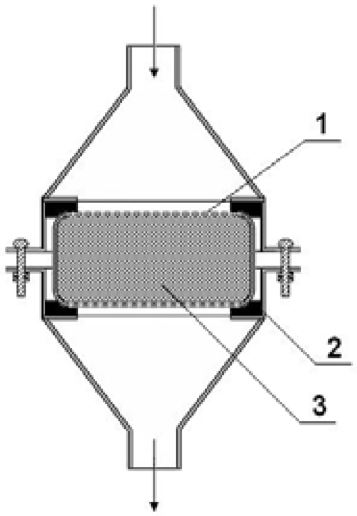
Air purification from carbon monoxide pollution for respiratory organs protection in extreme situations is very important problem. The most effective method for CO removal from air is catalytic oxidation, that's why many research works over last decades were dedicated to development of the novel catalysts for carbon monoxide oxidation.

Active heterogenized CO oxidation catalysts on the basis of fibrous carbon materials, manufactured at "Khimvolokno" ent. Svetlogorsk (Belarus), were synthesized in our laboratory. Catalysts were prepared by means of impregnation fibrous carbon plates (mean diameter 7,8 and 5,0 cm, fibrous carbon material carbopon) with acidified aqueous solution of palladium (II), copper (II) and iron (III) salts followed by drying and thermal activation.

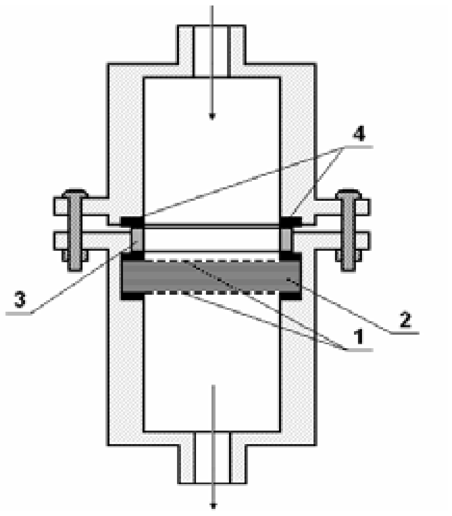
First type of reactor – model of respirator – was made on the basis of shell (volume for catalyst loading 100 cm^3, diameter 7,8 cm) from respirator RU-60M filter cell, manufactured by OOO "Briz-Kama" Vladimir (RU). Empty shell was loaded with 25 plates of fibrous carbon impregnated with salts solution to achieve maximum packing density. Then prepared filter cell was griped between flanges of two conical parts made of caprolon (Pic. 1).

Results of catalytic experiments on the model of respirator are shown at Table. Conversion of carbon monoxide at volume velocity of reaction mixture 9000 h^{-1} (0,03% of CO in air) is 94%. Full conversion of CO wasn't reached due to the leakages of carbon monoxide between catalyst and shell was concluded.

Thereupon second type of catalytic reactor was designed and created. This reactor contain ring gasket between flanges of upper and lower parts, which eliminate leakages of reaction mixture past catalyst.



Pic. 1



Pic. 2

Pic. 1. Scheme of the first type of catalytic reactor (model of respirator).
1 – shell of filter cell; 2 – gasket; 3 – catalyst.

Pic. 2. Scheme of the second type of catalytic reactor.
1 – holding sheet grids; 2 – catalyst; 3 – packing ring; 4 – rubber gaskets.

Table. Results of catalytic experiments on two types of reactors (catalysts prepared on the basis of nonwoven carbon material “carbopon B aktiv”; metal loadings, mass. %: 1,04 Pd; 5,15 Cu; 0,41 Fe; reaction mixture – 0,03% CO in air; testing temperature – 20°C, testing time – 10 min).

Diameter of reactor crosssection, cm	Vol. velocity, h^{-1}	Vol. of catalyst loading, cm^3	Contact time, c	Mass of catalyst loading, g	CO conver-sion, %	Specific activity, mkmol $CO/g_{cat} \cdot s$
First type of reactor (model of respirator)						
7,8	9011	100	0,4	15,04	94	0,195
Second type of reactor						
3,6	13654	13,2	0,25	2,35	99	0,274

Comparing results of catalytic experiments, shown in Table, one can see superiority in activity of the second type of reactor before the model of respirator even at higher volume velocity of the reaction mixture due to more dense packing which eliminates leakages of CO past catalyst.

LIST OF PARTICIPANTS

ABIEV Rufat
St. Petersburg State Institute of Technology
(Technical University)
Moskowskii pr., 26
190013 St. Petersburg
Russia
Tel: +7 812 494 9276
E-mail: rufat.abiev@gmail.com

AFANASENKO Vitaliy Gennadyevich
Ufa State Petroleum Technical University
Kosmonavtov str., 1
450062 Ufa
Russia
E-mail: awirus@rambler.ru

AGIRRE Ion
Faculty of Engineering of Bilbao
(University of the Basque Country)
Alameda Urquijo s/n
48013 Bilbao
Spain
E-mail: ion.agirre@ehu.es

AIOUACHE Farid
Queen's University Belfast
BT9 5AG Belfast
UK
E-mail: f.aiouache@qub.ac.uk

ALEKSEENKO Sergey Vladimirovich
Institute of Thermophysics SB RAS
Novosibirsk
Russia
E-mail: aleks@itp.nsc.ru

ALTSHULER Heinrich Naumovich
Kemerovo Department of the Institute of
Solid State Chemistry and
Mechanochemistry SB RAS
18, Sovetskii ave.
650099 Kemerovo
Russia
Tel: +7 384 2 36 3766
Fax: +7 384 2 21 1838
E-mail: sorbent@kemnet.ru

AMARA Mourad
Université des Sciences et de la Technologie
Houari-boumedienne
BP 32 El-Alia, Bab-Ezzouar
16111 Algiers
Algeria
Tel: +213 21 24-7311
Fax: +213 21 24 7311
E-mail: mo_amara@yahoo.fr

AMINOVA Guzel
Kazan State Technological University
ul. Karla Marksa, 68
420015 Kazan
Russia
Tel: +7 843 23 14 292
Fax: +7 843 23 14 211
E-mail: a_guzel@mail.ru

AMROUSSE Rachid
University of Poitiers
CNRS 6503 40 Avenue du Recteur Pineau F -
86022 POITIERS Cedex
France
E-mail: rachid.amrousse@univ-poitiers.fr

AMUTIO Maider
Universidad del País Vasco
48013 Bilbao
Spain
E-mail: maider.amutio@ehu.es

ANFIMOVA Natalya Petrovna
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Fax: +7 383 330 8056
E-mail: anf@catalysis.ru

ANTAL Steven Peter
Interphase Dynamics
33 Rosemere
12109 Troy
USA
Tel: (518) 395 6985
Fax: (518) 833 0219
E-mail: antals@rpi.edu

ARABIOURRUTIA Miriam
Universidad del País Vasco
480080 Bilbao
Spain
E-mail: miriam.arabiourrutia@ehu.es

ARACIL Jose
University of Complutense
28040 Madrid
Spain
E-mail: jam1@quim.ucm.es

ARJMAND Mehdi
Royal Institute of Technology (KTH)
Valhallavägen, 79
SE-100 44 Stockholm
Sweden
Tel: +46 8 7906000
Fax: +46 8 7906500
E-mail: mehdiarjmand@yahoo.com

ARKHIPOV Vladimir Afanasievich
Research Institute of Applied Mathematics and Mechanics of Tomsk State University
Lenina str., 36
634050 Tomsk
Russia
Tel: +7 3822 529 547
Fax: +7 3822 529 547
E-mail: leva@niipmm.tsu.ru

ARPORNWICHANOP Amornchai
Chulalongkorn University
10330 Bangkok
Thailand
E-mail: amornchai.a@chula.ac.th

ARUTYUNOV Vladimir Sergeevich
Semenov Institute of Chemical Physics RAS
Kosygina str., 4
119991 Moscow
Russia
E-mail: arutyunov@center.chph.ras.ru

AUTHAYANUN Suthida
Chulalongkorn University
10330 Bangkok
Thailand
E-mail: suthida_autt@hotmail.com

AVETISOV Alexander Konstantinovich
Karpov Institute of Physical Chemistry
Vorontsovo pole, 10
105064 Moscow
Russia
E-mail: avetisov@cc.nifhi.ac.ru

AVGOUROPOULOS George
Foundation for Research and Technology-Hellas (FORTH),
Institute of Chemical Engineering & High Temperature Chemical Processes (ICE-HT)
P.O. Box: 1414, Stadiou Str., Platani-Rio
GR-26504 Patras
Greece
E-mail: geoavg@iceht.forth.gr

AVVAKUMOV Evgeny Grigorievich
Institute of Solid State Chemistry and Mechanochemistry SB RAS
Kutateladze str., 18
630128 Novosibirsk
Russia
Tel: +7 383 332 86 83
Fax: +7383 332 28 47
E-mail: avvakumov@solid.nsc.ru

BABKIN Viatcheslav Stepanovich
Institute of Chemical Kinetics and Combustion of SB RAS
Institutskaya str., 3
630090 Novosibirsk
Russia
Tel: +7(383) 330 91 50
Fax: +7(383) 330 73 50
E-mail: babkin@kinetics.nsc.ru

BACHURIKHIN Alexander Leonidovich
N.D. Zelinsky Institute of Organic Chemistry RAS
119991 Moscow
Russia
E-mail: Shao-kahn@yandex.ru

BANKOVIĆ Predrag
Institute of Chemistry Technology and Metallurgy, Department of Catalysis and Chemical Engineering
Njegoševa, 12
11000 Belgrade
Serbia
E-mail: predragb@nanosys.ihtm.bg.ac.rs

BARAJAS Solano Andrés Fernando
Industrial University of Santander
Ciudad Universitaria, Cra 27 calle 9
AA678 Bucaramanga
Colombia
Tel: +57 7 634 4000
Fax: +57 7 645 4697
E-mail: andresfdobarajas@gmail.com

BARCLAY Donald
Autoclave Engineers Division,
Division of Snap-Tite Inc.
8325 Hessinger Drive
16509 Carnoustie
UK
Tel: +1 814 869 5700
Fax: +1 814 860 5811
E-mail: donald_barclay@snap-tite.com

BARRIO V. Laura
University of the Basque Country
48013 Bilbao
Spain
E-mail: laura.barrio@ehu.es

BASOV Nikolay Lukich
A.V. Topchiev Institute of Petrochemical Synthesis RAS
Leninskiy pr., 29
119991 Moscow
Russia
Tel: +7 (495) 954 4222
Fax: +7 (495) 633 8520
E-mail: basov@ips.ac.ru

BAWOLAK Katarzyna
Technical University of Lodz
ul. Zeromskiego 116
90-924 Lodz
Poland
E-mail: kbawolak@p.lodz.pl

BEKSAEV Sergey
Nordbiochem Ltd.
Kuuse 2
63303 Polva
Estonia
E-mail: sbeksaev@inbox.ru

BEN AMRANE Badrtamam
National Institute for Occupational Health and Safety, University of BATNA
05000 Batna
Algeria
E-mail: benambad@yahoo.fr

BEN TAHAR Nourredine
M'hamed Bougara University
35000 Boumerdès
Algeria
E-mail: nbentahardz@yahoo.fr

BENSAID Samir
Politecnico di Torino
corso Duca degli Abruzzi 24
10129 Torino
Italy
E-mail: samir.bensaid@polito.it

BIASI Pierdomenico
Åbo Akademi University
Biskopsgatan 8
20500 Turku
Finland
E-mail: bpierdom@abo.fi

BONDAN Ben-Hur
Training and Staff Development Branch, Organisation for the Prohibition of Chemical Weapons
Johan de Wittlaan 32
2517JR The Hague
The Netherlands
E-mail: trainingmgt@opcw.org

BORDES-RICHARD Elisabeth
Universite des Sciences et Technologies de Lille
Villeneuve d'Ascq
France
E-mail: Elisabeth.Bordes@univ-lille1.fr

BOSHENYATOV Boris Vladimirovich
Institute of Applied Mechanics RAS
Leninskii pr., 32
119991 Moscow
Russia
E-mail: bosbosh@mail.ru

BREITKOPF Cornelia
Department Mechanical Engineering, Institute of Power Engineering
Helmholtzstrase 14
01069 Dresden
Germany
Tel.: ++49 351 463 37621
E-mail: Cornelia.Breitkopf@tu-dresden.de

BRICKER Jeffery
UOP- A Honeywell Company
Chicago
USA
E-mail: jeffery.bricker@uop.com

BRUK Lev Grigor'evich
Moscow State Academy of Fine Chemical Technology
Vernadsky pr., 86
119571 Moscow
Russia
E-mail: lgbruk@mail.ru

BUNIMOVICH Grigori
Matros Technologies, Inc.
14963 Green Circle Dr., Chesterfield, MO 63017
63146 St. Louis
USA
Tel: +1 (314) 439 9699
Fax: +1 (314) 439 9950
E-mail: grigorii@matrostech.com

BYKOV Leonid
Institute of Problems of Chemical Physics RAS
pr. Akademika Semenova, 1
142432 Chernogolovka
Russia
Tel: +7(496 52) 24 476
Fax: +7(496) 515 54 20
E-mail: lbik@icp.ac.ru

BYKOV Valery
D. Mendeleyev University of Chemical Technology of Russia
9, Miusskaya square
125047 Moscow
Russia
Tel: +7 (499) 978 8733
Fax: +7 (495) 609 2964
E-mail: vibykov@mail.ru

CASTAÑO Pedro
University of the Basque Country, Faculty of Science and Technology
Sarriena S/N
48080 Bilbao
Spain
E-mail: pedro.castano@ehu.es

CASTILLO-ARAIZA Carlos O.
Universidad Autónoma Metropolitana-Iztapalapa
Av. Rafael Atlixco 186
09340 Mexico City
Mexico
E-mail: carlos.castilloaraiza@gmail.com

CATALDO Macarena
Politecnico di Torino
corso Duca degli Abruzzi 24
10129 Torino
Italy
E-mail: debora.fino@polito.it

CENTENO Felipe Orlando
Núcleo de Excelência em Geração Térmica e Distribuída –
NEST, Universidade Federal de Itajubá
Av. BPS, 1303 - Bairro: Pinheirinho
CEP: 37500 - Itajubá - MG
Brazil
Tel: +55 (35) 3629 1355
Fax: +55 (35) 3629 1355
E-mail: fcenteno@ingenieros.com

CHEN Jyh-Cherng
Hungkuang University
Taichung
Taiwan
E-mail: jcchen@sunrise.hk.edu.tw

CHEPELENKO Victor Nikolaevich
MZSS
Obrucheva str., 31
117246 Moscow
Russia
E-mail: v.chepelenko@mzss.ru

CHERNYKH Igor
Institute of Computational Mathematics and Mathematical Geophysics of SB RAS
pr. Akademika Lavrentieva, 6
630090 Novosibirsk
Russia
Tel: +7(383) 330 8353
Fax: +7(383) 330 8783
E-mail: chernykh@ssd.sscc.ru

CHISTOVALOV Sergey Mikhailovich
A.N. Nesmeyanov Institute of Organoelement Compounds RAS
Vavilov str., 28
119991 Moscow
Russia
Tel: +7 (499) 135 82 98
Fax: +7 (499) 135 50 85
E-mail: sm53@ineos.ac.ru

CHIVILIKHIN Michael
Corning Inc.
Shatelena str., 26 A
194021 St. Petersburg
Russia
E-mail: chivilikms@corning.com

CHORNAJA Svetlana
Riga Technical University
14/24 Azenes St.
LV 1006 Riga
Latvia
E-mail: svetlana@ktf.rtu.lv

CHUMACHENKO Victor Anatolievich
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Tel: +7(383) 330 8269
Fax: +7(383) 330 8056
E-mail: vachum@catalysis.ru

CORENGIA Pablo Andrés
INASMET-TECNALIA
Mikeletegi Pasealekua, 2 - Parque Tecnológico
E-20009 San Sebastian-Donostia
Spain
Tel: +34 943 003 700
Fax: +34 943 003 800
E-mail: pablo.corengia@inasmet.es

DANILEVICH Elena Vladimirovna
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Tel: +7 383 32 69 412
Fax: +7 383 330 8056
E-mail: yelenasem@catalysis.ru

DANILOVA Marianna Mikhaylovna
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Fax: +7 383 330 8056
E-mail: sabirova@catalysis.ru

DATSEVICH Leonid
The University of Bayreuth
Bayreuth
Germany
E-mail: datsevich@mpcp.de

DATTA Pradyot
Max Planck Institute for Dynamics of Complex Technical Systems
Sandtorstrasse 1
39106 Magdeburg
Germany
E-mail: datta@mpi-magdeburg.mpg.de

DAVLETBAEVA Ilsiya
Kazan State Technological University
ul. Karla Marksa, 68
420015 Kazan
Russia
Tel: +7 843 2314292
Fax: +7 843 2314211
E-mail: davletbaeva09@mail.ru

DE LOS REYES Jose Antonio
Universidad Autónoma Metropolitana-Iztapalapa
Av. Rafael Atlixco 186
09340 Iztapalapa
Mexico
E-mail: jarh@xanum.uam.mx

De WILD Paul J.
Energy Research Center of the Netherlands
Westerduinweg, 3
1755 Petten
The Netherlands
E-mail: dewild@ecn.nl

DIAKONOV German
Kazan State Technological University
Karla Marksa str., 68
420015 Kazan
Russia
Tel: +7 843 2 314 292
Fax: +7 843 2 314 211
E-mail: guerman@kstu.ru

DIEZ Fernando valeriano
University of Oviedo
Oviedo
Spain
E-mail: fds@uniovi.es

DOGU Gulsen
Gazi University
Chemical Engineering
Ankara
Turkey
E-mail: gdogu@gazi.edu.tr

DOGU Timur
Middle East Technical University
Chemical Engineering Department
06531 Ankara
Turkey
E-mail: tdogu@metu.edu.tr

DOLGANOV Igor Mikhailovich
Tomsk Polytechnic University
pr. Lenina, 30
634050 Tomsk
Russia
Tel: +7 (3822) 56 3470
Fax: +7 (3822) 56 3865
E-mail: dolganovim@sibmail.com

DOMINGUEZ-Ramos Antonio
University of Cantabria, Department of
Chemical Engineering
Avda. Los Castros, s.n.
39005 Santander
Spain
E-mail: domingueza@unican.es

ECHEANDIA Sergio
"National biotechnology company" LLC
Moscow, Vernadskogo pr., 84
117506 Bilbao
Spain
Tel: +7(495) 231 7958
Fax: +7(495) 231 2259
E-mail: sergio.echeandia@ehu.es

ELOKHIN Vladimir
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Tel: +7(383) 330 8269
Fax: +7(383) 330 8056
E-mail: elokhin@catalysis.ru

ELORDI Gorka
University of the Basque Country,
Faculty of Science and Technology
Sarriena S/N
48080 Bilbao
Spain
E-mail: gorka.elordi@ehu.es

ERKOC Ertugrul
TU Dresden
Dresden
Germany
E-mail: ertugrul.erkoc@tu-dresden.de

ESCAMILLA Eleazar Máximo
Instituto Tecnológico de Celaya
Ave. Tecnológico y Antonio García Cubas S/N
38010 Celaya
Mexico
Tel: +52(461) 61 17575
Fax: +52 (461) 61 17744
E-mail: eleazar.escamilla@itcelaya.edu.mx

FARHAT Kamal
University of Poitiers
CNRS 6503 40 Avenue du Recteur Pineau F
86022 POITIERS Cedex
France
E-mail: kamal.farhat@univ-poitiers.fr

FEDOROVA Zaliya Amirovna
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Fax: +7(383) 330 8056
E-mail: sabirova@catalysis.ru

FEFELOV Vasiliy Fedorovich
Omsk State Technical University
pr. Mira, 11
644000 Omsk
Russia
Tel: +7 3812 652 379
Fax: +7 3812 652 379
E-mail: Fefelov_Vasiliy@mail.ru

FINASHINA Elena Dmitrievna
N.D. Zelinsky Institute of Organic
Chemistry RAS
119991 Moscow
Russia
E-mail: finesta@mail.ru

FINO Debora
Politecnico di Torino
corso Duca degli Abruzzi 24
10129 Torino
Italy
E-mail: debora.fino@polito.it

FLID Mark Rafailovich
Scientific Research Engineering Centre "SYNTEZ"
Vernadsky pr., 86
119571 Moscow
Russia
Tel: +7(495) 434 8544
Fax: +7(495) 434 8153
E-mail: mflid@yandex.ru

FRANTSINA Evgeniya Vladimirovna
Tomsk Polytechnic University
pr. Lenina, 30
634050 Tomsk
Russia
Tel: +7 (3822) 563470
Fax: +7 (3822) 563865
E-mail: evf86@sibmail.com

FRUSTERI Francesco
Institue for Advanced Technologies for Energy "Nicola Giordano"
Via S. Lucia sopra Contesse, 5
98127 Messina
Italy
Tel: +39 090 624233
Fax: +39 090 624247
E-mail: francesco.frusteri@itae.cnr.it

GAIDAI Natalia Alexandrovna
N.D. Zelinsky Institute of Organic Chemistry RAS
119991 Moscow
Russia
E-mail: gaidai@server.ioc.ac.ru

GAMERO Mónica
University of the Basque Country,
Faculty of Science and Technology
Sarriena S/N
48080 Bilbao
Spain
E-mail: mgyenes@hotmail.com

GAREA Aurora
University of Cantabria, Department of Chemical Engineering
Avda. Los Castros, s.n.
39005 Santander
Spain
E-mail: gareaa@unican.es

GARCIA Paulo Perez
Training and Staff Development Branch,
Organisation for the Prohibition of Chemical Weapons
Johan de Wittlaan 32
2517JR The Hague
The Netherlands
E-mail: trainingmgt@opcw.org

GIORNO Lidietta
Institute on Membrane Technology, ITM-CNR
C/o Unical, Via P. Bucci 17/C
87030 Rende CS
Italy
E-mail: l.giorno@itm.cnr.it

GOLAVLEVA Anna Vladimorovna
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Tel: +7 383 330 9750
Fax: +7 383 330 9687
E-mail: gav@catalysis.ru

GOMES Vincent G
University of Sydney
School of Chemical and Biomolecular Engineering
NSW 2006 Sydney
Australia
Tel: 612 9351 4868
Fax: 612 9351 2854
E-mail: vincent.gomes@sydney.edu.au

GONZALEZ Angel Dario
Industrial University of Santander
Ciudad Universitaria, Cra 27 calle 9
AA678 Bucaramanga
Colombia
Tel: 634 4000
Fax: 645 4697
E-mail: andagon@gmail.com

GONZÁLEZ Bello Orlando José
INASMET-TECNALIA
Mikeletegi Pasealekua, 2 - Parque Tecnológico
E-20009 San Sebastián
Spain
Tel: +34 943 003 700
Fax: +34 943 003 800
E-mail: orlando.gonzalez@inasmet.es

GOODWIN Gary
Autoclave Engineers Division,
Division of Snap-Tite Inc.
8325 Hessinger Drive
16509 Carnoustie
UK
E-mail: donald_barclay@snap-tite.com

GORBENKO Tatiana Ivanovna
Tomsk State University
Lenina str., 36
634050 Tomsk
Russia
E-mail: leva@niipmm.tsu.ru

GORBUNOV Vitaly
Omsk State Technical University
pr. Mira, 11
644000 Omsk
Russia
Tel: +7 3812 652 379
Fax: +7 3812 652 379
E-mail: Vitaly_Gorbunov@mail.ru

GORODSKY Sergey Nikolaevich
Moscow State Academy of Fine
Chemical Technology
Vernadsky pr., 86
119571 Moscow
Russia
E-mail: Gorodsky@yandex.ru

GORRI Daniel
University of Cantabria, Department of
Chemical Engineering
Avda. Los Castros, s.n.
39005 Santander
Spain
E-mail: gorrie@unican.es

GORŠEK Andreja
University of Maribor, Faculty of Chemistry and
Chemical Engineering
Smetanova 17
SI-2000 Maribor
Slovenia
E-mail: andreja.gorsek@uni-mb.si

GRECHISHKINA Olga
D.I. Mendeleev University of Chemical
Technology of Russia
Miusskaya square, 9
125047 Moscow
Russia
Tel: +7 499 978 9589
Fax: +7 499 978 9554
E-mail: olgrech@hotmail.com

GUBANOVA Elena Leonidovna
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Tel: +7(383) 330 8269
Fax: +7(383) 330 8056
E-mail: lgekster@gmail.com

GUILLEN Donna Post
Idaho National Laboratory Idaho Falls
83415 Idaho
USA
Tel: (208) 526 1744
E-mail: Donna.Guillen@inl.gov

GUMEROV Askhat
Kazan State Technological University
Karla Marksa str., 68
420015 Kazan
Russia
Tel: +7 843 231 4292
Fax: +7 843 231 4211
E-mail: Gumerov_a@mail.ru

GYNGAZOVA Maria Sergeevna
Tomsk Polytechnic University
pr. Lenina, 30
634050 Tomsk
Russia
Tel: +7 (3822) 56 3470
Fax: +7 (3822) 56 3865
E-mail: gyngazova@mail.ru

HAASE Stefan
Technische Universität Dresden
01062 Dresden
Germany
E-mail: stefan.haase@tu-dresden.de

HAIDER Muhammad Hasnain
Cardiff University
CF10 3AT Cardiff
UK
E-mail: haidermh@cardiff.ac.uk

HANIKA Jiri
Institute of Chemical Process Fundamentals,
Czech Academy of Sciences
Rozvojova 135
16502 Prague
Czech
E-mail: hanika@icpf.cas.cz

HARTMANN Vladimir Leonidivich
LLC "NIAP-KATALIZATOR"
Svyazi, 10
301660 Novomoskovsk
Russia
Tel: +7 48762 716 29
Fax: +7 48762 71818
E-mail: vhart@yandex.ru

HEERES Erik
University of Groningen, Department of
Chemical Engineering
Nijenborgh 4
9747 AG Groningen
The Netherlands
E-mail: h.j.heeres@rug.nl

HERNÁNDEZ Carucci José Rafael
Åbo Akademi University,
Laboratory of Industrial Chemistry
Biskopsgatan 8
20500 Turku
Finland
E-mail: johernan@abo.fi

HERNANDEZ Simelys
Italian Institute of Technology
Corso Duca degli Abruzzi 24
10129 Torino
Italy
E-mail: simelys.hernandez@iit.it

HOSEN Mohammad Anwar
University of Malaya
50603 Kuala Lumpur
Malaysia
Tel: + 60379676897
E-mail: anwar.buet97@yahoo.com

HUSEYNOVA Farida Kamil
M.F. Nagiyev Institute of Chemical
Problems NAS
of Azerbaijan
29, H. Javid avenue
Az1143 Baku
Azerbaijan
Tel: +99412 439 38 71
Fax: (994 12) 438 7756, (994 12) 438 9765
E-mail: farida_az@inbox.ru

IGARASHI Akira
Kogakuin University
Hachioji-shi
192-0015 Tokyo
Japan
E-mail: igarashi@cc.kogakuin.ac.jp

ILUSHKA Igor
Nordbiochem Ltd.
Kuuse 2
63303 Polva
Estonia
E-mail: agro3000@inbox.ru

ISMAGILOV Zinfer Rishatovich
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Tel: +7 383 32 69 412
Fax: +7383 330 8056
E-mail: zri@catalysis.ru

IVANOV Evgeniy
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5,
630090 Novosibirsk
Russia
Tel: +7 383 32 69 412
Fax: +7383 330 8056
E-mail: eugene@catalysis.ru

IVANOVA Avigeya Nikolaevna
Institute of Problems of Chemical Physics RAS
Acad. Semenov av., 1
142432 Chernogolovka
Russia
Tel: +7 496 522 4476
Fax: +7 496 515 5420
E-mail: ivanova@icp.ac.ru

JASO Stanislav Miloslav
Dynamik und Betrieb Technischer Anlagen,
Berlin Institute of Technology
Strasse des 17. Juni 135, Sekr. KWT9
10619 Berlin
Germany
Tel: +49 303 126 900
Fax: +49 303 142 6915
E-mail: stanislavjaso@mailbox.tu-berlin.de

JIMENEZ Nuria
Technical University of Catalonia
Av. Diagonal, 647
08028 Barcelona
Spain
E-mail: nuria.divins@gmail.com

JOGUNOLA Olatunde
Åbo Akademi University, Laboratory of
Industrial Chemistry
Biskopsgatan 8
20500 Turku
Finland
E-mail: jolatund@abo.fi

JORDI Robin Guy
Sasol Technology Research and Development
1 Klasie Havenga Road, Sasolburg, Orange
Free State
1947 Sasolburg
South Africa
E-mail: robin.jordi@sasol.com

JOZWIAK Wojciech Kazimierz
Technical University of Lodz
ul. Zeromskiego 116
90-924 Lodz
Poland
E-mail: wjozwiak@p.lodz.pl

KAFAROV Vyacheslav
Industrial University of Santander
Ciudad Universitaria, Cra 27 calle 9
AA678 Bucaramanga
Colombia
Tel: 57 7 634 4746
Fax: 57 7 635 540
E-mail: kafarov@uis.edu.co

KAGYRMANOVA Aygana
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Fax: +7383 330 8056
E-mail: aigana@catalysis.ru

KAPUSTIN Vladimir Mikhailovich
OAO VNIPIneft, Gubkin Russian State Oil &
Gas University
Engels str. 32
105005 Moscow
Russia
Tel. +7 495 795 31 32
Fax: +7 916 650 4437
E-mail: vkapustin@VNIPIneft.ru

KARAKAYA Mustafa
Department of Chemical Engineering
Bogazici University
34342 Istanbul
Turkey
E-mail: mustafa1907@gmail.com

KAZAKOV Dmitriy Alexandrovich
Perm State Technical University
Komsomolskiy pr., 29
614990 Perm
Russia
Tel: +7 (342) 219 8283
Fax: +7 (342) 219 8475
E-mail: kazakovbiotech@mail.ru

KHANIKYAN Vago
D. Mendeleyev University of Chemical
Technology of Russia
9 Miusskaya square
125047 Moscow
Russia
Tel: +7 (499) 978 8733
Fax: +7 (495) 609 2964
E-mail: vagokhan@rambler.ru

KHLOPOV Dmitry
D. Mendeleyev University of Chemical
Technology of Russia
9, Miusskaya square
125047 Moscow
Russia
Tel: +7 (499) 978 8733
Fax: +7 (495) 609 2964
E-mail: hlopovd@mail.ru

KIRILIN Alexey Viktorovich
Åbo Akademi University
Biskopsgatan, 8
20500 Turku/Åbo
Finland
E-mail: akirilin@abo.fi

KIRYUKHIN Dmitry Pavlovich
Institute of Problems of Chemical Physics RAS
pr. Akademika Semenova, 1
142432 Chernogolovka
Russia
E-mail: kir@icp.ac.ru

KLENOV Oleg Pavlovich
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Tel: +7(383) 330 8269
Fax: +7(383) 330 8056
E-mail: klen@catalysis.ru

KOLB Gunther
Institute für Mikrotechnik Manz GmbH
Carl-Zeiss-Straße, 18-20
55129 Mainz
Germany
Tel: +49 6131 990301
Fax: +49 6131 990305
E-mail: miesch@imm-mainz.de

KOLESNIKOV Andrei
Tshwane University of Technology
Private Bag X680 Pretoria 0001
Republic of South Africa
0001 Pretoria
South Africa
Tel: +27 12 382 3512
Fax: +27 12 382 3532
E-mail: kolesnikova@tut.ac.za

KOPTYUG Igor V.
Institute "International Tomografic
Center" of SB RAS
Institutskaya str., 3
630090 Novosibirsk
Russia
Tel: +7(383) 333 1448
Fax: +7(383) 333 1399
E-mail: koptyug@tomo.nsc.ru

KORNEEV Igor
D. Mendeleyev University of Chemical
Technology of Russia
9, Miusskaya square
125047 Moscow
Russia
Tel: +7 (499) 978 8733
Fax: +7 (495) 609 2964
E-mail: iskorneev8282@mail.ru

KOROBITSYNA Ludmila Leonidovna
Institute of Petroleum Chemistry of SB RAS
3, Akademicheskiy Ave.
634021 Tomsk
Russia
Tel: +7(382 2) 491623
Fax: +7(382 2) 491457
E-mail: kll@ipc.tsc.ru

KORSUNSKIY Boris Lvovich
Institute of Problems of Chemical Physics RAS
pr. Akademika Semenova, 1
142432 Moscow
Russia
E-mail: kors36@mail.ru

KOVÁCS Sándor
University of Pannonia, Institute of Chemical
and Process Engineering,
Department of Hydrocarbon
and Coal Processing
Egyetem u. 10, P.O.Box.158
H-8201 Veszprém
Hungary
E-mail: kovacss@almos.uni-pannon.hu

KOZHEVNIKOV Ivan
University of Liverpool,
Department of Chemistry
L69 7ZD Liverpool
UK
E-mail: kozhev@liverpool.ac.uk

KOZLOVA Ekaterina
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Tel: +7(383) 330 8269
Fax: +7(383) 330 8056
E-mail: kozlova@catalysis.nsk.su

KOZLOVSKIY Ivan
D. Mendeleyev University of Chemical
Technology of Russia
9, Miusskaya square
125047 Moscow
Russia
Tel: +7 (499) 978 8733
Fax: +7 (495) 609 2964
E-mail: iakozlovsky@rambler.ru

KOZLOVSKIY Roman
D. Mendeleyev University of Chemical
Technology of Russia
9, Miusskaya square
125047 Moscow
Russia
Tel: +7 (499) 978 8733
Fax: +7 (495) 609 2964
E-mail: rakozlovskiy@mail.ru

KUCHEROV Alexei Viktorovich
N.D. Zelinsky Institute of Organic
Chemistry RAS
119991 Moscow
Russia
E-mail: akuchero2004@yahoo.com

KUKUEVA Vitalina
Academy of Fire Safety named
after Chernobyl Heroes
Cherkassy
Ukraine
E-mail: kukueva@yahoo.com

KUMAR Ghodke praveen
National Institute of Technology Tirchy
620015 Tirchy
India
E-mail: gkumarouct@gmail.com

KUSEMA Bright T
Åbo Akademi University,
Laboratory of Industrial Chemistry
Biskopsgatan, 8
20500 Turku
Finland
E-mail: bright.kusema@abo.fi

KUVSHINOV Gennady
Novosibirsk State Technical University
K. Marx pr., 20
630092 Novosibirsk
Russia
Tel: +7 383 346 0843
Fax: +7 383 346 0209
E-mail: gennady.kuvshinov@gmail.com

KUZ'MIN Alexey
A.V. Topchiev Institute of Petrochemical
Synthesis RAS
Leninskiy pr., 29
119991 Moscow
Russia
Tel: +7 (495) 954 4222
Fax: +7 495) 633 8520
E-mail: kuzmin@ips.ac.ru

KUZMIN Andrey O.
Boreskov Institute of Catalysis SB RAS
630090 Novosibirsk
Russia
Fax: +7 383 330 8056
E-mail: kuzmin@catalysis.ru

KUZNETSOV Sergey A.
Institute of Chemistry and Technology
of Rare Elements
and Mineral Raw Materials RAS
(Kola Science Centre)
26, Akademgorodok
184209 Apatity
Russia
Tel: +7 (81555) 79136
Fax: +7 (81555) 61658
E-mail: kuznet@chemy.kolasc.net.ru

LAGUSSEVA Elena Ivanovna
Tver Technical University
A. Nikitina str., 22
170026 Tver
Russia
E-mail: lagusseva@yandex.ru

LAPIN Nikolaj
Institution of Russian Academy
of Sciences Institute of Microelectronic
Technology and High-
Purity Materials RAS
Chernogolovka
Russia
Tel: +7 (496) 524 4015
Fax: +7 (495) 962 8047
E-mail: lapin@iptm.ru

LEBEDEVA Valentina Ivanovna
A.V. Topchiev Institute of Petrochemical
Synthesis RAS
Leninskiy pr., 29
119991 Moscow
Russia
Tel: +7(495) 954 4222
Fax: +7 (495) 633 8520
E-mail: lebedeva@ips.ac.ru

LEDESMA Cristian
Technical University of Catalonia
Av. Diagonal, 647
08028 Barcelona
Spain
E-mail: cristian.ledesma@upc.edu

LEINO Ewelina
Åbo Akademi University,
Laboratory of Industrial Chemistry
Biskopsgatan, 8
20500 Turku
Finland
E-mail: ewleino@abo.fi

LEVEC Janez
University of Ljubljana/
National Institute of Chemisty
SI-1001 Ljubljana
Slovenia
E-mail: janez.levec@ki.si

LI Ben
Department of Chemical Engineering,
Vrije Universiteit Brussel
Pleinlaan 2
1050 Brussels
Belgium
Tel: 02 629 17 99
Fax: 02 629 32 48
E-mail: benli@vub.ac.be

LI Hui
Energy research Center of the Netherlands
NL1755ZG Petten
Netherlands
E-mail: li@ecn.nl

LIKHOLOBOV Vladimir Alexandrovich
Institute of Hydrocarbons
Processing of SB RAS
644040 Omsk
Russia
E-mail: val@ihcp.oscsbras.ru

LITVAK Egor
Tomsk Polytechnic University
pr. Lenina, 30
634050 Tomsk
Russia
Tel: +7 (3822) 56-34-70
Fax: +7 (3822) 56-38-65
E-mail: litvak_egor@mail.ru

LLORCA Jordi
Technical University of Catalonia
Av. Diagonal, 647
08028 Barcelona
Spain
E-mail: jordi.llorca@upc.edu

LÖFBERG Axel
Universite des Sciences et
Technologies de Lille
Villeneuve d'Ascq cedex
France
E-mail: Axel.Lofberg@univ-lille1.fr

LOPES João
University of Porto
Porto
Portugal
E-mail: deq07006@fe.up.pt

LOPEZ-Isunza Felipe
Universidad Autónoma Metropolitana-
Iztapalapa
Av. Rafael Atlixco, 186
09340 Mexico City
Mexico
E-mail: felipe@xanum.uam.mx

LOPONOV Konstantin
University of Warwick
Coventry
UK
E-mail: k.n.loponov@warwick.ac.uk

LUKIANOV Boris Nikolaevich
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Tel: +7(383) 330 8269
Fax: +7(383) 330 8056
E-mail: lukjanov@catalysis.ru

LUSS Dan
University of Houston
77204 Houston
USA
E-mail: Dluss@mail.uh.edu

LYSIKOV Anton Igorevich
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Tel: +7(383) 330 8269
Fax: +7(383) 330 8056
E-mail: lyanig@catalysis.ru

MAKARFI Yusuf Isa
Research Institute for Physico-Chemical
Medicine, Federal Medico-Biological Agency
Pirogovskaya str., 1a
119992 Moscow
Russia
Tel: +7 495 246 4311
Fax: +7 495 246 4501
E-mail: yusufisa@yahoo.com

MAKAROV Alexandr Mihailovich
ZAO ECAT
Professora Dedukina 27
614013 Perm
Russia
Tel: +7 342 2 714249
Fax: +7 342 2 391339
E-mail: mak_perm@mail.ru

MAKAROV Mikhail
D. Mendeleyev University of Chemical
Technology of Russia
9, Miusskaya square
125047 Moscow
Russia
Tel: +7 (499) 978 8733
Fax: +7 (495) 609 2964
E-mail: mgm_dist@mail.ru

MAKARSHIN Lev Lvovich
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Tel: +7 383 32 69 412
Fax: +7 383 330 8056
E-mail: makarshin@catalysis.ru

MAKHLIN Vladilen Abramovich
A.V. Topchiev Institute of Petrochemical
Synthesis RAS
Leninskiy prospect, 29
119991 Moscow
Russia
Tel: +7 (495) 954 4222
Fax: +7 (495) 633 8520
E-mail: makhlin@ips.ac.ru

MÄKI-ARVELA Päivi
Åbo Akademi University
Biskopsgatan, 8
20500 Turku
Finland
E-mail: paivi.maki-arvela@abo.fi

MALINOV Vladimir Ivanovich
Russian Federal Nuclear Center – All-Russian
Scientific Research
Institute of Experimental Physics
FSUE RFNC - VNIIEF
Mira Ave, 37
607188 Sarov, Nizhny Novgorod region
Russia
E-mail: assa@astra.vniief.ru

MAMEDOV Eldar Musa
Institute of chemical problems of NAS of
Azerbaijan
29, Huseyn Javid Ave., Baku, AZ1143,
Azerbaijan
Baki
Azerbaijan
Tel: (99412) 4394159
E-mail: chemproblem@mail.ru

MANIECKI Tomasz Przemyslaw
Technical University of Lodz
ul. Zeromskiego, 116
90-924 Lodz
Poland
E-mail: tmanieck@p.lodz.pl

MANUJKO Galia
Kazan State Technological University
Karla Marksa str., 68
420015 Kazan
Russia
Tel: +7 843 231 4292
Fax: +7 843 231 4211
E-mail: a_guzel@mail.ru

MARÍN Pablo
University of Oviedo
E-33006 Oviedo
Spain
E-mail: marinpablo@uniovi.es

MATROS Yurii
Matros Technologies, Inc.
63017 St.Louis
USA
E-mail: yurii@matrostech.com

MATROSOVA Maria Mikhailovna
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
E-mail: himitsu08@mail.ru

MATVEEV Pavel Valerievich
Russian Federal Nuclear Center – All-Russian
Scientific Research
Institute of Experimental Physics
FSUE RFNC - VNIIEF
Mira Ave, 37
607188 Sarov, Nizhny Novgorod region
Russia

MIER Diana
Universidad del País Vasco
48013 Bilbao
Spain
E-mail: diana.mier@ehu.es

MIERCZYNSKI Pawel
Technical University of Lodz
ul. Zeromskiego, 116
90-924 Łódź
Poland
E-mail: mierczyn25@wp.pl

MISHANIN Sergey Vladimirovich
Russian Federal Nuclear Center – All-Russian
Scientific Research
Institute of Experimental Physics
FSUE RFNC - VNIIEF
Mira Ave, 37
607188 Sarov, Nizhny Novgorod region
Russia
E-mail: mishanin@front.ru

MITINA Ludmila Mikhailovna
International Science and Technology Center
Krasnoproletarskaya str., 32-34
127473 Moscow
Russia
E-mail: mitina@istc.ru

MITYANINA Olga Evgenievna
Tomsk Polytechnic University
pr. Lenina, 30
634050 Tomsk
Russia
Tel: +7 (3822) 56 3470
Fax: +7 (3822) 56 3865
E-mail: elvoreth@mail.ru

MOREIRA del Rio Jesus
The University of Western Ontario
N6A 5B9 London
Canada
E-mail: jmoreira@uwo.ca

MTHOMBENI Bongani
University of Cape Town
Rondebosch
7701 Cape Town
South Africa
Tel: +272 1650 2518
Fax: +272 1650 5501
E-mail: bongani.mthombeni@uct.ac.za

MULYASHOV Sergey
Nordbiochem Ltd.
Kuuse 2
63303 Polva
Estonia
E-mail: lab-tos@mail.ru

MUZRIN Dmitry
Åbo Akademi University
Biskopsgatan, 8
20500 Turku
Finland
E-mail: dmurzin@abo.fi

MYRZALIYEVA Saule
National Center on Complex Processing of
Mineral Raw
Materials of the Republic of Kazakhstan RSE
Zhandosov str., 67
050036 Almaty
Kazakhstan
E-mail: saulekerchaiz@mail.ru

NAKANO Katshuyuki
Department of Chemical Engineerig,
Fukuoka University
8-19-1 Nakakuma Jonan-ku, Fukuoka
814-0180 Fukuoka
Japan
Tel: +81 92 871 6631
Fax: +81 92 865 6031
E-mail: knakano@pop06.odn.ne.jp

NAKANO Ryoko
Department of Energy and Environment
Systems,
Faculty of Engineering, Fukuoka University
8-19-1 Nanakuma, Jonan-ku,
814-0180 Fukuoka
Japan
E-mail: td095503@cis.fukuoka-u.ac.jp

NAZARKINA Roza Alexandrovna
Ministry of Education and Science RF
Tverskaya str., 11
103906 Moscow
Russia
Tel.: +7 495 629 0394
E-mail: Zagranka07@mail.ru

NEKHAMKINA Olga
Department of Chemical Engineering,
Institute of Technology, Technion
Technion City
32000 Haifa
Israel
Tel.: +972 482 93561
Fax: +972 482 95672
E-mail: aermwon@tx.technion.ac.il

NIKACEVIC Nikola
Delft University of Technology
Mekelweg 2
2628 CD Delft
The Netherlands
E-mail: n.nikacevic@tudelft.nl

NIKOLAEV Yevgeny Anatolyevich
Ufa State Petroleum Technical University
Kosmonavtov str., 1
450062 Ufa
Russia
E-mail: nikevan@rambler.ru

NOGIN Yurii Nikolaevich
Rostbiochem Ltd
Timakova str., 4
630117 Novosibirsk
Russia
Tel: +7 383 332 4137
Fax: +7 383 332 8042
E-mail: nogin@rbchem.ru

NOSKOV Alexander
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Tel: +7 383 330 6878
Fax: +7 383 330 6878
E-mail: noskov@catalysis.ru

OBALI Zeynep
Middle East Technical University
Chemical Engineering Department
06531 Ankara
Turkey
E-mail: z_obali@yahoo.com

OBUCHI Eiko
Department of Chemical Engineering,
Fukuoka University
8-19-1 Nakakuma Jonan-ku, Fukuoka
814-0180 Fukuoka
Japan
Tel: +81 92 871 6631
Fax: +81 92 865 6031
E-mail: eobuchi@fukuoka-u.ac.jp

OJEDA Karina
Universidad Industrial de Santander,
Chemical Engineering Department
Cra 27 Cl 9
A.A. 678 Bucaramanga
Colombia
E-mail: kaojeda@gmail.com

ONSAN Zeynep Ilsen
Department of Chemical Engineering,
BOGAZICI University
Bebek
34342 Istanbul
Turkey
Tel: +90 212 359 7024
Fax: +90 212 287 2460
E-mail: onsan@boun.edu.tr

OVCHINNIKOVA Elena Victorovna
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Tel: +7 383 330 8210
Fax: +7 383 330 8056
E-mail: evo@catalysis.ru

PAI Zinaida Petrovna
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Tel: +7 383 32 69 412
Fax: +7 383 330 8056
E-mail: zpai@catalysis.ru

PAKHARUKOV Ilya
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Fax: +7 383 330 8056
E-mail: ilyapakharukov@yandex.ru

PALMISANO Pietro
Politecnico di Torino
corso Duca degli Abruzzi 24
10129 Torino
Italy
E-mail: pietro.palmisano@polito.it

PAPADAKI Maria I.
Department Of Environmental &Natural
Resources Management
SEFERI 2
GR30100 Agrinio
Greece
Tel: +30 264 107 4184
Fax: +30 264 1074 176
E-mail: m.papadaki@leeds.ac.uk

PAPAVASILIOU Joan
Foundation for Research and Technology-
Hellas (FORTH),
Institute of Chemical Engineering &
High Temperature Chemical
Processes (ICE-HT)
P.O. Box: 1414, Stadiou Str., Platani-Rio
GR-26504 Patras
Greece
E-mail: jpapav@iceht.forth.gr

PARAKHIN Oleg Afanasievich
NPK SINTEZ
Sotsialisticheskii pr., 87
56049 Barnaul
Russia
E-mail: parakhin@cintez.org

PARFENOVA Elena Aleksandrovna
Peter Huber Kältemaschinenbau GmbH
Werner-von-Siemens str., 1
77656 Offenburg
Germany
Tel: +49 781 96030
Fax: +49 781 57211
E-mail: ep@huber-online.com

PATMAR Edison
Chuvash State University
Moskovskii pr., 15
428015 Cheboksary
Russia
E-mail: edi75@mail.ru

PAVLOV Yurii
INNOVATIKA
pr. Mira, 119-69
129223 Moscow
Russia
Tel: +7 (495) 961 2012
E-mail: ypexpo@gmail.com

PÉCAR Darja
University of Maribor, Faculty of Chemistry and
Chemical Engineering
Smetanova, 17
SI 2000 Maribor
Slovenia
E-mail: darja.pecar@uni-mb.si

PECHENEGOV Yurii Yakovlevich
Saratov State Technical University
city of Engels,
Svobody square, 17
413100 Saratov
Russia
E-mail: mxp@techn.sstu.ru

PECHYEN Chiravoot
Kasetsart University
10900 Bangkok
Thailand
E-mail: kraterb@hotmail.com

PERKO David
National Institute of Chemistry
SI-1001 Ljubljana
Slovenia
E-mail: david.perko@ki.si

PESKOV Nikolay Vladimirovich
Department of Computational Mathematics & Cybernetics,
Lomonosov Moscow State University
Lenynskie Gory
119899 Moscow
Russia
E-mail: peskov@cs.msu.ru

PHILLIPS Lennie
Training and Staff Development Branch,
Organisation for the Prohibition of Chemical Weapons
Johan de Wittlaan 32
2517JR The Hague
The Netherlands
E-mail: trainingmgt@opcw.org

PINAEVA Larisa Gennadievna
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Tel: +7(383) 330 8269
Fax: +7(383) 330 8056
E-mail: pinaeva@catalysis.ru

PIVOVAROVA Irina Vladimorovna
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5,
630090 Novosibirsk
Russia
Tel: +7 383 330 6878
Fax:+7(383) 330 8056
E-mail: noskov@catalysis.ru

PLATA Chávez Vladimir
Universidad Industrial de Santander,
Chemical Engineering Department
Cra 27 Cl 9
A.A. 678 Bucaramanga
Colombia
E-mail: vladimirplata@gmail.com

PODLESNAYA Maria Vladimirovna
A.V. Topchiev Institute of Petrochemical Synthesis RAS
Leninskiy pr., 29
119991 Moscow
Russia
Tel: +7 (495) 954 4222
Fax: +7 (495) 633 8520
E-mail: podlesnaya@ips.ac.ru

POKROVSKAYA Svetlana Afanasievna
Boreskov Instutute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Tel: +7 383 330 8269
Fax: +7 383 330 8056
E-mail: pokrov@catalysis.ru

POLCZMANN Gyorgy
University of Pannonia, Institute of Chemical and Process Engineering
Egyetem u. 10, P.O.Box.158
H-8201 Veszprem
Hungary
E-mail: polczmann@almos.uni-pannon.hu

POPOK Evgeny
Tomsk Polytechnic University
pr. Lenina, 30
634050 Tomsk
Russia
Tel: +7 (3822) 563470
Fax: +7 (3822) 563865
E-mail: evgen-san@inbox.ru

POTEMKIN Dmitriy Igorevich
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Tel: +7 383 326 9412
Fax: +7383 330 8056
E-mail: potema@catalysis.ru

PROKHOROV Alexiy
D. Mendeleyev University of Chemical Technology of Russia
9, Miusskaya square
125047 Moscow
Russia
Tel: +7 (499) 978 8733
Fax: +7 (495) 609 2964
E-mail: proxorov.al@mail.ru

PRYMYSKA Svitlana
National Technical University of Ukraine (KPI)
03056 Kiev
Ukraine
E-mail: prymyska@ukr.net

RAIMONDI Andrea
Politecnico di Torino
corso Duca degli Abruzzi 24
10129 Turin
Italy
E-mail: andrea.raimondi@polito.it

RASRENDRA C.B.
University of Groningen
Nijenborg 4 9747 AG Groningen
The Netherlands
E-mail: c.b.rasrendra@rug.nl

RATTANAPHANEE Panarat
Suranaree University of Technology
School of Chemical Engineering
SUT 111 University Ave. Suranaree
30000 Nakhorn Ratchasima
Thailand
Tel: +66 4422 4591
Fax: +66 4422 4609
E-mail: panarat@sut.ac.th

REBOLLAR Moises
Instituto De Investigaciones Y Desarrollo Industrial
Oriente 101 3605
Col Río Blanco
07850 DF **Mexico**
E-mail: mrebollar@inidi.org

REBROV Evgeny
Eindhoven University of Technology
Den Dolech 2
5612AZ Eindhoven
The Netherlands
E-mail: e.rebrov@tue.nl

REDDY PRASAD Donipathi Mogili
Universiti Malaysia Pahang
Gambang, Kuantan, Pahang
26300 Kuantan
Malaysia
Tel: +609-549 2854
Fax: +609-549 2889
E-mail: dmrprasad@gmail.com

REDEKOP Evgeniy
Washington University in St. Louis
One Brookings Drive, Campus Box 119
63130-4899 St. Louis, MO
USA
E-mail: e_redekop@yahoo.com

REMIRO Aingeru
University of the Basque Country
Alameda Urquijo s/n
48013 Bilbao
Spain
E-mail: aingeru.remiro@ehu.es

RESHETNIKOV Sergey Ivanovich
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Tel: +7(383) 330 8269
Fax: +7(383) 330 8056
E-mail: reshet@catalysis.ru

REZNICHENKO Svetlana
St. Petersburg State Institute of Technology (Technical University)
Moskowskii pr., 26
190013 St. Petersburg
Russia
Tel: +7 812 494 9276
E-mail: cbeta.p@mail.ru

RING Zbigniew
BP Advanced Refining
Chicago
USA
E-mail: Zbigniew.Ring@bp.com

ROMANOVA Anastasiya
D. Mendeleyev University of Chemical Technology of Russia
9, Miusskaya square
125047 Moscow
Russia
Tel: +7 (499) 978 8733
Fax: +7 (495) 609 2964
E-mail: liceistka2003@mail.ru

ROMANOVSKY Rostislav Vladimirovich
Tomsk Polytechnic University
pr. Lenina, 30
634050 Tomsk
Russia
Tel: +7 (3822) 56 3470
Fax: +7 (3822) 56 3865
E-mail: ravix@sibmail.com

ROZANOVA Elena
Semyenov Institute of Chemical Physics RAS
Kosygina str., 4
119991 Moscow
Russia
E-mail: gav@catalysis.ru

RUDIN Vsevolod Nikolaevich
Lomonosov Moscow State University
Leninskie Gory
119991 Moscow
Russia
E-mail: bozh@radio.chem.msu.ru

RUSSO Nunzio
Politecnico di Torino
Corso Duca degli Abruzzi 24
10129 Torino
Italy
E-mail: nunzio.russo@polito.it

RUTIGLIANO L.
Politecnico di Torino
corso Duca degli Abruzzi 24
10129 Torino
Italy
E-mail: debora.fino@polito.it

RYNKOWSKI Jacek
Technical University of Lodz
ul. Zeromskiego 116
90-924 Łódź
Poland
E-mail: jacryn@p.lodz.pl

RYZHKINA Irina Sergeevna
A.E. Arbuzov Institute of Organic and Physical Chemistry KazRC RAS
Akademika Arbuzova str., 8
420088 Kazan
Russia
Tel: +7 (843) 231 9170
Fax: +7 (843) 275 2253
E-mail: ryzhkina@iopc.knc.ru

SAADI Adel
Université des Sciences et de la Technologie
Houari-boumedienne
BP 32 El-Alia, Bab-Ezzouar
16111 Algiers
Algeria
Tel: +213-21-24-73-11
Fax: +213-21-24-73-11
E-mail: adel_saadi@yahoo.fr

SADEGHI Mohammad Taghi
Iran University of Science and Technology
(IUST)
Narmak, 16846 Tehran
Iran
Tel: +98 21 7724 0496
Fax: +98 21 7724 0495
E-mail: sadeghi@iust.ac.ir

SADOVSKAYA Ekaterina Michailovna
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Fax: +7(383) 330 8056
E-mail: sadovsk@catalysis.ru

SADYKOV Vladislav Alexandrovich
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Fax: +7(383) 330 8056
E-mail: sadykov@catalysis.nsk.su

SAHIN Serap
Åbo Akademi University, Laboratory of
Industrial Chemistry
Biskopsgatan, 8
20500 Turku
Finland
E-mail: ssahin@abo.fi

SALAEV Mikhail Anatol'evich
Tomsk State University
Lenina str., 36
634027 Tomsk
Russia
E-mail: mihan555@yandex.ru

SAN JOSE Maria J.
University of the Basque Country,
Faculty of Science and Technology
Sarriena S/N
48080 Bilbao
Spain
E-mail: mariajose.sanjose@ehu.es

SÁNCHEZ Eduardo
Universidad Industrial de Santander,
Chemical Engineering Department
Cra 27 Cl 9
A.A. 678 Bucaramanga
Colombia
E-mail: sancheztuiran@gmail.com

SANS SANGORRIN Victor
University of Warwick
Coventry
UK
E-mail: V.Sans-Sangorrin@warwick.ac.uk

SANTACESARIA Elio
University of Naples Federico II
Complesso di M.te S. Angelo Via Cintia
80126 Naples
Italy
E-mail: elio.santacesaria@unina.it

SARBAK Zenon
Adam Mickiewicz University
60780 Poznań
Poland
E-mail: sarbak@amu.edu.pl

SCHOUTEN Jaap C.
Eindhoven University of Technology
Den Dolech 2
5612AZ Eindhoven
The Netherlands
E-mail: j.c.schouten@tue.nl

SELISHCHEV Dmitry Sergeevich
Novosibirsk State University
Pirogova str., 2
630090 Novosibirsk
Russia
E-mail: selishev@catalysis.ru

SEMYANISTIJ Aleksej Vladimirovich
Institute of Applied Mechanics RAS
Leninskii pr., 32
119991 Moscow
Russia
E-mail: bosbosh@mail.ru

SERMON Paul Anthony
University of Surrey
Stag Hill
GU2 7XH Guildford
UK
Tel: 00441483689593
E-mail: p.sermon@surrey.ac.uk

SEZGI Naime Asli
Middle East Technical University
Chemical Engineering Department
06531 Ankara
Turkey
E-mail: sezgi@metu.edu.tr

SHAROVA Ekaterina Sergeevna
Tomsk Polytechnic University
pr. Lenina, 30
634050 Tomsk
Russia
Tel: +7 (3822) 56 3470
Fax: +7 (3822) 56 3865
E-mail: sharova@sibmail.com

SHEIKH Munir Ahmed
Training and Staff Development Branch,
Organisation for the Prohibition of Chemical Weapons
Johan de Wittlaan 32
2517JR The Hague
The Netherlands
E-mail: trainingmgt@opcw.org

SHEINTUCH Moshe
Institute of Technology, Technion
Technion City
32000 Haifa
Israel
E-mail: cermsll@tx.technion.ac.il

SHELEPOVA Ekaterina Vladimirovna
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Tel: +7(383) 330 8269
Fax: +7(383) 330 8056
E-mail: shev@catalysis.ru

SHMACHKOVA Vera Petrovna
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Tel: +7 383 330 8210
Fax: +7 383 330 8056
E-mail: veras@catalysis.ru

SHNIDOROVA Irena Olegovna
Tomsk Polytechnic University
pr. Lenina, 30
634050 Tomsk
Russia
Tel: +7 (3822) 563470
Fax: +7 (3822) 563865
E-mail: shnidorova@sibmail.com

SHTERTSER Natalya Vladimirovna
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Fax: +7 383 330 8056
E-mail: nat@catalysis.ru

SHUBINA Larisa
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Fax: +7 383 330 8056
E-mail: shubina@catalysis.ru

SHULAYEV Nickolay Sergeyevich
Ufa State Petroleum Technical University
Kosmonavtov str., 1
450062 Ufa
Russia
E-mail: nshulayev@rambler.ru

SHVETS Valeriy Fedorovich
D. Mendeleyev University of Chemical Technology of Russia
9, Miusskaya square
125047 Moscow
Russia
Tel: +7 (499) 978 8733
Fax: +7 (495) 609 2964
E-mail: shvets@muctr.ru

SIDOROVA Olga Ivanovna
Tomsk State University
Lenina str., 36
634027 Tomsk
Russia
E-mail: sidorova@xf.tsu.ru

SIMAGINA Valentina Ilinichna
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Fax: +7 383 330 8056
E-mail: simagina@catalysis.ru

SIMAKOV Valeriy
Institute of Thermophysics of SB RAS
pr. Akademika Lavrentieva, 1
630090 Novosibirsk
Russia
Tel: +7(383) 330 7050
Fax: +7(383) 330 8480
E-mail: sova3d@mail.ru

SIMAKOVA Irina Leonidovna
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Fax: +7 383 330 8056
E-mail: simakova@catalysis.ru

SIMAKOVA Olga Andreevna
Åbo Akademi University
Biskopsgatan, 8
20500 Turku/Åbo
Finland
E-mail: olga.simakova@abo.fi

SINEV Mikhail
Semenov Institute of Chemical Physics RAS
Kosygina str., 4
119991 Moscow
Russia
E-mail: sinev@chph.ras.ru

SLINKO Marina Mikhailovna
Semenov Institute of Chemical Physics RAS
Kosygina str., 4
119991 Moscow
Russia
E-mail: slinko@polymer.chph.ras.ru

SNYTNIKOV Pavel Valerievich
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Tel: +7 383 330 8210
Fax: +7 383 330 8056
E-mail: pvsnyt@catalysis.ru

SOLOVYEV Evgeniy
Novosibirsk State Technical University
K. Marx prospect, 20
630092 Novosibirsk
Russia
Tel: +7 383 346 0843
Fax: +7 383 346 0209
E-mail: easoloviov@mail.ru

SOONGPRASIT Kanit
Chulalongkorn University
10330 Bangkok
Thailand
E-mail: kapanda_soong@hotmail.com

STAROVEROV Dmitry V
D. Mendeleyev University of Chemical
Technology of Russia
9, Miusskaya square
125047 Moscow
Russia
Tel: 8-499-9788839
E-mail: stardv@pxty.ru

STEFANIDIS Georgios
Delft University of Technology
Leeghwaterstraat, 44
2628 CA Delft
The Netherlands
Tel: +31 15 2786678
E-mail: g.stefanidis@tudelft.nl

STEPANEK Jan
Institute of Chemical Technology, Prague
Technicka 5
16628 Prague
Czech
Tel: +42 02204 44159
E-mail: jan.stepanek@vscht.cz

STISHENKO Pavel V
Omsk State Technical University
pr. Mira, 11
644000 Omsk
Russia
Tel: +7 (3812) 652379
Fax: +7 (3812) 652379
E-mail: PavelStishenko@yandex.ru

STITT Hugh
Johnson Matthey Catalysts
Billingham
Cleveland, TS23 1LB
UK
E-mail: hugh.stitt@matthey.com

STRIZHAK Peter
L.V. Pisarzhevsky Institute of Physical
Chemistry NAS of Ukraine
pr. Nauki, 31
03028 Kiev
Ukraine
E-mail: pstrizhak@hotmail.com

SU Fangzheng
Max-Planck institute of Colloid and Interface
14476 Potsdam
Germany
E-mail: fangzheng.su@mpikg.mpg.de

SUBHASH H. Risbud
Stanford University
USA
E-mail: shrisbud@ucdavis.edu

SUCHKOV Yury
D. Mendeleyev University of Chemical
Technology of Russia
9, Miusskaya square
125047 Moscow
Russia
Tel: +7 (499) 978 8733
Fax: +7 (495) 609 2964
E-mail: yrp97@yandex.ru

SUGANO Motoyuki
Nihon University, College of Science and
Technology
1-5, Kanda Surugadai, Chiyoda-ku
1010062 Tokyo
Japan
Tel: +81 3 3259 0809
Fax: +81 3 3293 7572
E-mail: sugano@chem.cst.nihon-u.ac.jp

SUGURBEKOVA Gulnara
M.Kh. Dulaty Taraz State University
Kazakhstan, Taraz c., Tole by Str, 60
080012 Taraz
Kazakhstan
Tel: +7(7262) 455997
Fax: +7(7262) 453664
E-mail: gulnar-sugur@yandex.ru

SUH Dong Jin
Korea Institute of Science and Technology
39-1 Hawolgok-dong Seongbuk-gu
136-791 Seoul
Korea (South)
E-mail: djsuh@kist.re.kr

SULIMOV Aleksandr
Dzerzhinsk Polytechnic Institute
(branch of R.Y. Alekseev Nizhny Novgorod
State Technical University)
Dzerzhinsk
Russia
E-mail: asulimov@mail.ru

SULMAN Esfir Mikhailovna
Tver Technical University,
Institute of Nano and Biotechnologies
A. Nikitina str., 22
170026 Tver
Russia
E-mail: sulman@online.tver.ru

SULMAN Mikhail
Tver Technical University,
Institute of Nano and Biotechnologies
A. Nikitina str., 22
170026 Tver
Russia
E-mail: sulman@online.tver.ru

SUSLOV Aleksei
High Current Electronics Institute SB RAS
pr. Academicheskii, 4
634055 Tomsk
Russia
Tel: +7(382 2) 491544
Fax: +7(382 2) 492410
E-mail: suslov@to.hcei.tsc.ru

TAGAWA Tomohiko
Department of Chemical Engineering,
Nagoya University
Furo-cho, Chikusa-ku
464-8603 Nagoya
Japan
Tel: 052 789 3388
E-mail: tagawa@nuce.nagoya-u.ac.jp

TAGIYEV Dilgam
Institute of Petrochemical Processes of
Azerbaijan NAS
AZ1025 Baku
Azerbaijan
E-mail: dtagiyev@hotmail.com

TEMKIN Oleg Naumovich
Moscow State Academy of Fine Chemical
Technology
Vernadsky pr., 86
119571 Moscow
Russia
E-mail: olegtemkin@mail.ru

THOTLA Suman
Max Planck Institute for Dynamics
of Complex Technical Systems
Sandtorstrasse, 1
39106 Magdeburg
Germany
E-mail: thotla@mpi-magdeburg.mpg.de

TIKHONOVA Margarita Vladimirovna
Institute of Petrochemistry and Catalysis RAS
pr. Oktyabrya, 141
450075 Ufa
Russia
E-mail: tiny_daisy@mail.ru

TOMAS Igor Alexeevich
Rostbiochem Ltd.
Timakova str., 4
630117 Novosibirsk
Russia
Tel: +7 383 332 4137
Fax: +7 383 332 8042
E-mail: tomas@rbchem.ru

TOMASH Michael Alexandrovich
Priasov State Technical University
Mariupol
Ukraine
E-mail: syncma@mvs.net.ua

TOMASZEWSKA Karina Anna
Technical University of Lodz
ul. Zeromskiego, 116
90-924 Łódź
Poland
E-mail: karinatom@poczta.onet.pl

TRACHUK Anton Vladimirovich
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Fax: +7 383 330 8056
E-mail: trachuk@ngs.ru

TRUSHKOV Yuriy Yurivich
ZAO Ventmontagh
Sibirskaya str., 1
614000 Perm
Russia
Tel: +7 834 210 1521
Fax: +7 834 226 2636
E-mail: vnmg@yandex.ru

TSVETKOV Oleg Nikolaevich
All-Russian Research Institute
of Oil Refining, JSC
6, Aviamotornaya str.
111116 Moscow
Russia
Tel: +7 499 763 5629
Fax: +7 495 361 1285
E-mail: paom@rambler.ru

UDALOV Evgeniy Igorevich
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Fax: +7 383 330 8056
E-mail: udalov@catalysis.ru

VAN GEEM Kevin M.
Ghent University,
Laboratory for Chemical Technology
Krijgslaan 281, S5
9000 Ghent
Belgium
E-mail: kevin.vangeem@ugent.be

VERNIKOVSKAYA Nadezhda Viktorovna
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Tel: +7(383) 330 8269
Fax: +7(383) 330 8056
E-mail: vernik@catalysis.ru

VICENTE Jorge
University of the Basque Country,
Faculty of Science and Technology
Sarriena S/N
48080 Bilbao
Spain
E-mail: jorge.vicente@ehu.es

VOSKOBOYNIKOV Timur
UOP LLC
50 East Algonquin Rd,
Des Plaines, IL 60017-5016
USA
E-mail: Timur.Voskoboynikov@uop.com

VOSMERIKOVA Liudmila Nikolaevna
Institute of Petroleum Chemistry of SB RAS
Akademicheskiy pr., 3
634021 Tomsk
Russia
Tel: +7(382-2) 49 1623
Fax: +7(382-2) 49 1457
E-mail: lkplu@ipc.rsc.ru

VYATKIN Yury Leonidovich
D. Mendeleyev University
of Chemical Technology of Russia
9, Miusskaya square
125047 Moscow
Russia
Tel: +7 499 978 8839
E-mail: yuris-vtk@mtu-net.ru

WIERZBA Ida
University of Calgary,
Schulich School of Engineering
2500 University Drive N.W.
T2N 1N4 Calgary
Canada
E-mail: iwierzba@ucalgary.ca

YAAKOB Zahira
National University of Malysia
Department of Chemical and Process
Engineering
43600 Bangi
Malaysia
Tel: +60 3 8921 6400
Fax: +60 3 8921 6148
E-mail: zahira@eng.ukm.my

YAKOVLEV Vadim Anatolevich
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrenteva, 5
630090 Novosibirsk
Russia
Tel: +7 383 330 6254
Fax: +7(383) 330 8056
E-mail: yakovlev@catalysis.ru

YUDINA Elena Stanislavovna
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Tel: +7(383) 330 8269
Fax: +7(383) 330 8056
E-mail: yudina@catalysis.ru

YUZIN Gleb Igorevich
Presidium of SB RAS
pr. Akademika Lavrentieva, 17
630090 Novosibirsk
Russia
Tel: +7(383) 330 0567
Fax: +7(383) 330 1062, 330 1846
E-mail: ovc@sbras.nsc.ru

ZAGORUIKO Andrey Nikolaevich
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Tel: +7 383 330 8210
Fax: +7 383 330 8056
E-mail: zagor@catalysis.ru

ZAKHAROV Vladimir Pavlovich
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Fax: +7 383 330 8056
E-mail: xap@catalysis.ru

ZAMUDIO Espinoza Miguel Angel
Politecnico di Torino
corso Duca degli Abruzzi 24
10129 Turin
Italy
E-mail: miguel.zamudio@polito.it

ZAMULINA Tatiana Vladimirovna
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Tel: +7 383 330 6297
Fax: +7 383 330 8056
E-mail: zam@catalysis.ru

ZHAPBASBYEV Uzak Kairbekovich
Kazakh-British Technical University
59, Tole-Bi str.
050000 Almaty
Kazakhstan
Tel: +7(7272) 504655
Fax: +7(727) 3334175
E-mail: U.Zhapasbayev@kbtu.kz

ZHIZHINA Elena Georgievna
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Fax: +7 383 330 8056
E-mail: zhizh@catalysis.ru

ZHOU Xing-Gui
East China University of Science and Technology
130 Meilong Road
200237 Shanghai
China
E-mail: xgzhou@ecust.edu.cn

ZHU Zhirong
Tongji University, Department of Chemistry
200092 Shanghai
China
Tel: 00862 16509 2563
Fax: 00862 16598 1097
E-mail: zhuzhirong@tongji.edu.cn

ZHUKOVA Olga
Siberian State Technology University
Krasnoyarsk
Russia
E-mail: zhukovolga@yandex.ru

ZOLOTARSKII Ilya
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Tel: +7 383 3269 412
Fax: +7 383 330 8056
E-mail: zol@catalysis.ru

ZUEVA Julia Nikolaevna
Institute of Problems of Chemical Physics RAS
pr. Akademika Semenova, 1
142432 Chernogolovka
Russia
E-mail: sam@icp.ac.ru

ZUEVSKAYA Anna Evgenievna
Ministry of the Industry and Trade of the Russian Federation
Kitaigorodskii proezd, 7
109074 Moscow
Russia
E-mail: Zuevskaya@minprom.gov.ru

ŽUNIĆ Marija
Institute of Chemistry Technology and Metallurgy, Department of Catalysis and Chemical Engineering
Njegoševa, 12
11000 Belgrade
Serbia
E-mail: marija.zunic@nanosys.ihtm.bg.ac.rs

ZUÑIGA Jon
INASMET-TECNALIA
Mikeletegi Pasealekua, 2 - Parque Tecnológico
San Sebastián
Spain
Tel: +34 943 003 700
Fax: +34 943 003 800
E-mail: jon.zuniga@inasmet.es

ZYRYANOVA (POPOVA) Maria Michailovna
Boreskov Institute of Catalysis SB RAS
pr. Akademika Lavrentieva, 5
630090 Novosibirsk
Russia
Tel: +7(383) 330 8269
Fax: +7(383) 330 8056
E-mail: popovamm@catalysis.ru

CONTENT

ORAL PRESENTATIONS
SECTION I

ORAL PRESENTATIONS

SECTION III Chemical Reactors and Technologies for Emerging Applications

POSTER PRESENTATIONS
SECTION III

XIX International Conference on Chemical Reactors

CHEMREACTOR-19

Editors: Professor Alexander S. Noskov
Dr. Andrey N. Zagoruiko

The abstracts are printed as presented, and all responsibilities we address to the authors. Some abstracts underwent a correction of misprints and rather mild editing procedure.

Compiler: Tatiana V. Zamulina

Computer processing of text: Natalia A. Tsygankova

Cover design: Nina F. Poteryaeva

Disk maker : Aleksey A. Spiridonov

Подписано в печать 24.08.2010 Формат 60x84/8
Усл. печ. л. 80 Заказ N Тираж 250

Отпечатано на полиграфическом участке издательского отдела
Института катализа им. Г.К. Борескова Сибирского отделения РАН
Россия, 630090, Новосибирск, проспект Академика Лаврентьева, 5.