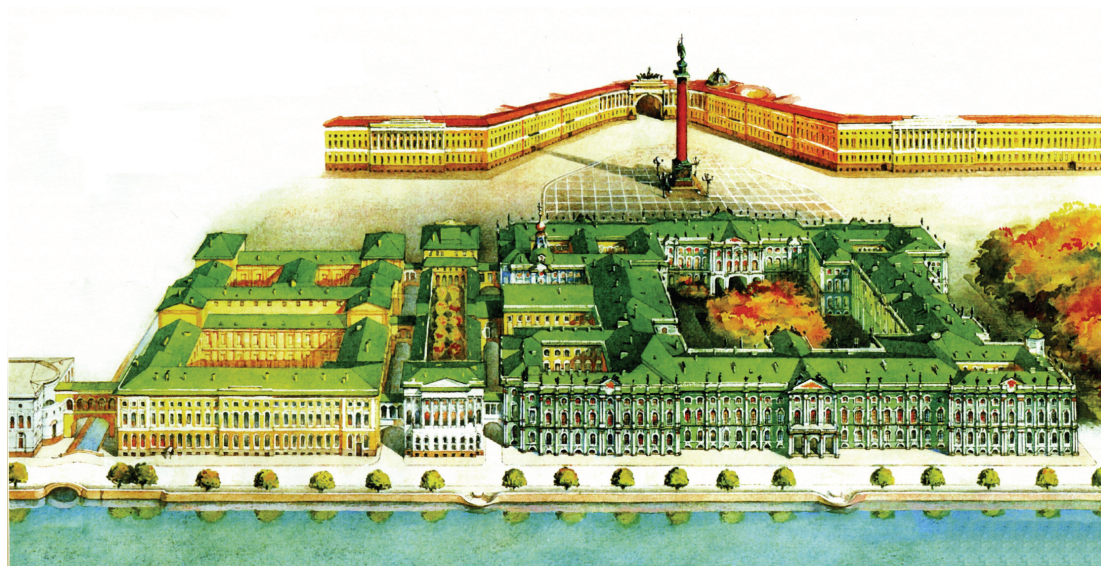


**Boreskov Institute of Catalysis SB RAS
Indian Institute of Technology – Madras**



**IV Russian-Indian Symposium
on Catalysis and Environmental Engineering**

ABSTRACTS

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Тезисы докладов IV Российско-Индийского симпозиума
«Каталитические технологии для защиты окружающей среды»

Сборник включает тезисы ключевых лекций и устных докладов по направлениям:

- Катализ для утилизации нетрадиционных промышленных отходов и возобновляемых энергетических ресурсов
- Каталитические технологии защиты окружающей среды, включая переработку промышленных отходов и выхлопы транспорта
- Каталитическая конверсия биомассы в топливо и химические вещества
- Наноструктурированные катализаторы для химических процессов и защиты окружающей среды.

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KEYNOTE LECTURES

KL-1 ÷ KL-13

Science & Engineering of Pores, Particles and Interfaces in Development of Green Processes

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I have been fascinated by phenomena occurring at the boundaries which has grown over the years with confluence of chemical and biological sciences and engineering, the formation of nanoparticles, pores and the interfaces residing within them. On one hand, network models and percolation processes in reservoir rocks, enhanced oil recovery and coal gasification, hydrogen generation to the finer aspects of multiphase reaction engineering and Green Chemistry. There is a very interesting thread among this areas which can be broadly viewed as Science & Engineering of Pores, Particles and Interfaces to develop clean and green processes, whether physical, chemical or biological or otherwise.

In recent years, my group has been working in three different areas of Green Chemistry using heterogeneous chemical catalysis, biocatalysis and phase transfer catalysis. New opportunities for the conversion of glycerol into value-added chemicals have emerged in recent years as a result of glycerol's unique structure, properties, bioavailability, and renewability. Different reaction pathways for selective catalytic conversion of bioglycerol into commodity chemicals include oxidation, hydrogenation (commonly called hydrogenolysis), dehydration, pyrolysis and gasification, steam reforming, thermal reduction into syngas, transesterification, etherification, oligomerization, polymerization, acetalization and carbonylation. The development of novel solid acids, bases, hydrogenation and oxidation catalysts for glycerol conversion will be discussed with examples. A recent area of great interest includes synthesis of enantiopure drugs, separation of racemic mixture and biocatalytic synthesis of fine chemicals. Our work encompasses different approaches to synthesize important pharmaceutical intermediates to overcome the limitations of conventional organic synthesis methods. Immobilized lipases were employed to study some pharmaceutically important reactions, under enzyme catalysis and microwave irradiation including development of kinetic models.

The liquid-liquid phase transfer catalyzed reaction can be intensified by converting it into three-liquid phases. An attractive process for the production of mandelic acid is through

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reaction between benzaldehyde, sodium hydroxide and chloroform in the presence of polyethylene glycol 4000 as a phase transfer catalyst. We address the modeling of a well-stirred reactor for the foregoing process in which organic droplets surrounded by a thin film of catalyst-rich phase are suspended in the aqueous phase. A population balance model is formulated L-L-L PTC reaction and solved by Monte Carlo simulation using interval of quiescence technique. Transport processes and intrinsic reaction kinetics are extracted from the experiments. This population balance model serves to assess and interpret the relative roles of various processes in L-L-L PTC reaction, such as diffusive transport, reaction and interaction between dispersed phase droplets. The model is expected to be an effective tool for reactor design and scale up.

Design of Catalytic Processes for Biofuels Production from Bio-Oil and Plant Oils

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Keywords: bio-oil, biodiesel, transesterification, hydrodeoxygenation, hydrotreatment, catalyst

1. Introduction

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 ir retrievable 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. But, 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.

2. Development of heterogeneous catalysts for plant oils transesterification

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 transesterification and mild hydrocracking sequentially [1,2].

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 transesterification catalysts under 200-220°C and 2.0 MPa and possibility of multiple catalyst

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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 H₂) and possibility of green diesel production with different cetane number via hydroisomerization catalysts application [3].

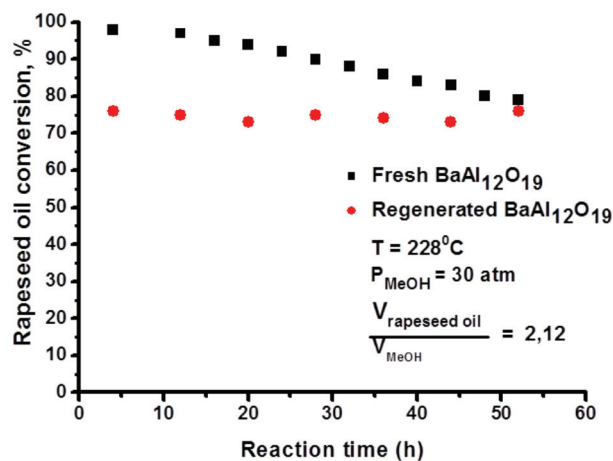


Fig. 1. Fresh and regenerated BaAl₁₂O₁₉ catalysts performance for transesterification of plant oils (biodiesel production). Catalyst was regenerated in the air atmosphere at 700°C for 3 h.

It was found (via XPS data) fresh BaAl₁₂O₁₉ catalyst has two forms of active components – strong-bond centers and weak-bond centers which were removed from catalyst surface during first cycle. After regeneration catalyst was showed constant activity in target process (Fig. 1).

3. Ni-based hydrotreatment catalysts for bio-oil upgrading

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. The main goal of the hydrotreatment of bio-oil is to reduce the content of oxygen that is responsible for such negative properties of bio-oil as high viscosity, non-volatility, aggressivity, immiscibility with mineral oil, instability, and tendency to polymerization.

In general, the most promising approach in the hydrotreatment of bio-oil is a two-stage hydrotreatment at high pressures of hydrogen (5 – 10 MPa). In this case, the first stage at 150 – 250°C consists in the partial deoxygenation of bio-oil components, which increases the thermal stability of partially deoxygenated products during their further hydrotreatment at higher temperatures 300–380°C.

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.

This technological scheme of bio-oil upgrade process includes liquefaction of biomass, fractionation, hydrodeoxygenation (HDO) of lignin-rich fraction with following co-processing in petroleum refinery.

On the first step the catalyst optimization included active components composition improvement. It was found that Ni-Cu solid solution is promising active component which reduce coke formation and leaching of active components in bio-oil HDO, increase yield of liquid hydrogenated products in comparison of commercial alone Ni-catalysts. Indeed preparation and testing in target processes such binary catalytic systems has shown that developed mild hydrocracking catalysts permit 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 [2].

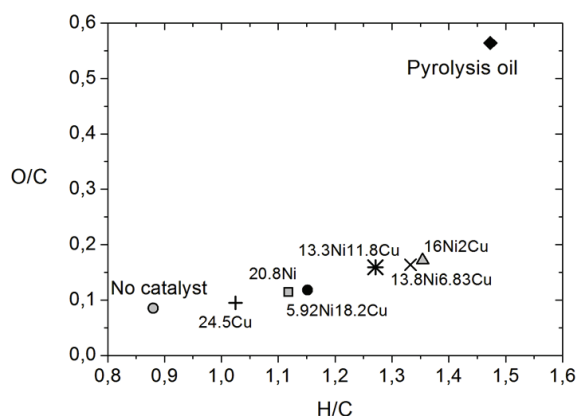


Fig. 2. Van Krevelen diagram for the products obtained in HDO of bio-oil over NiCu / Al₂O₃ catalysts at 11 MPa H₂ and temperatures 150 °C (for 1 h) and 350 °C (for 3 h).

It was shown (Fig.2) that the increase in the Ni content in a sample (except 20.8Ni) leads to an increase in the H/C ratio in the reaction products, which is a positive factor for the bio-oil hydrotreatment, because of the lower viscosity and molecular weight of the products. The increase in the ratio H/C indicates an increase in the activity of tested samples in hydrogenation [4]. The same effect was observed for HDO of anisole.

4. Conclusions

The new type of transesterification catalysts were proposed which possess high thermal and mechanical stability in biodiesel production process.

Concerning bio-oil hydrotreatment catalysts development the situation is not harmless. Some attempts have been made to find a new type of catalysts that would be inexpensive and free from the disadvantages of current catalysts. These efforts were oriented onto nickel systems. However, nickel systems are known for fast coking at high temperatures. On the other hand, a decrease in the process temperature to 150 – 250°C would results in dissolution of the nickel phase in reaction products, because oxidized nickel on the catalyst surface does not undergo unassisted reduction at such temperatures. This induces a problem of a modification of nickel

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catalysts with various additives to decrease the reduction temperature of a nickel-containing phase to the temperatures of the target reaction [5]. Besides, there is a necessity to stabilize the active nickel-containing component on a support by some specific preparation methods and/or by addition of some stabilizing agents in order to increase the overall thermal stability of the catalyst, because the features of bio-oil as a hydrotreatment reagent would result in fast coking (and hence deactivation) of any catalyst. The high thermal stability of the HDO catalysts is also necessary for repeated regeneration without loss in activity. An additional requirement to the HDO catalysts is the stability of their supports against hydrothermal treatment in an acidic medium.

The main approach to these problems is modification of nickel systems with Cu, Mo, La, Co, Fe, B, or P. At that, researchers focused on the use of stable supports (C, ZrO₂, TiO₂, SiO₂) or try to totally exclude a support. The recent trends in the development of the catalysts for bio-oil hydroforming suggest that the development of new catalysts for the bio-oil HDO will be intensified with a focus on unsulfided systems. A successful development of nickel-containing systems is to stimulate such branches of bioenergetics as production of liquid petrols from wood, edible and nonedible oilseed crops, or microalgae lipids.

5. Acknowledgements

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Transition Metal Catalysts for Olefin Polymerizations: Novel Polymer Structures and Functional Polymers

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Polyolefins constitute one of the largest and widely used polymers. They are generally inexpensive and the diversity of structures, and hence, properties that one can access using a wide variety of transition metal complexes make this area of study a fascinating subject in polymer science.

Our interest in this area is currently focused on two aspects. One, rational design of transition metal catalysts to produce ultrahigh molecular weight poly (ethylene)s and, second, to synthesize functional polymers with well-defined end functionalities.

The lecture will present some results from our ongoing research in this area. Novel Group IV transition metal complexes based on titanium and zirconium with open frameworks has been found to lead to very high molecular weight polyethylenes. Ability to control molecular weights in such polymerization has remained a challenge. We have studied the efficacy of arylsilanes to promote silanolytic chain transfer in ethylene polymerization using bis [N (3-tert-butylsalicylidene) 2,3,4,5,6-pentafluoroanilato] titanium (IV) dichloride as catalysts. A novel P-C-N-C-P framework capable of forming a six member chelate with nickel (II) and palladium (II) has been studied for ethylene and norbornene polymerization. The nickel complexes promote linear polymerization of ethylene without any “chain walking” process.

An approach to the synthesis of succinic anhydride terminated polyethylene has been studied. Such polyolefins with reactive functionality can be used to make novel copolymers, especially with long chain aliphatic diol monomers derived from biorenewable resources.

Glimpses of results from ongoing research in these areas will be presented.

Biorefinery of Lignocellulosic Biomass Based on the Integration of Heterogeneous Catalysis Processes

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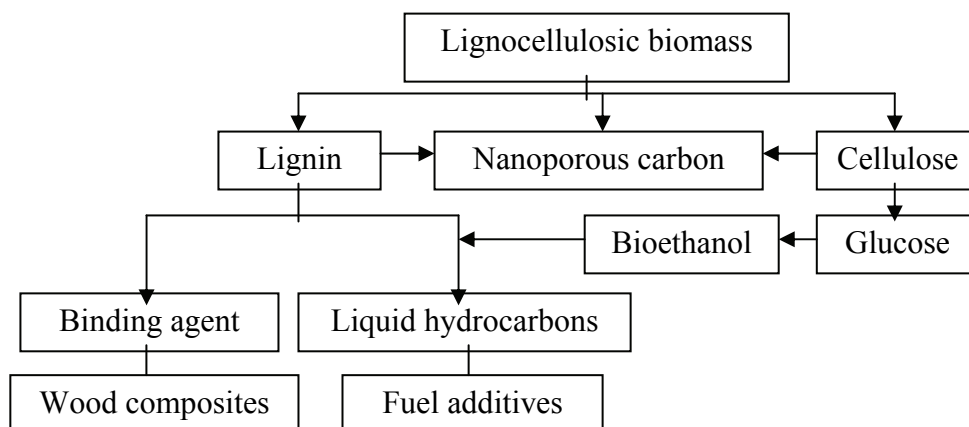
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The main drawbacks of conventional methods of lignocellulosic biomass processing are their lower productivity and selectivity as compared to petrochemical technologies. The successful development of the petrochemical industry can be attributed to an application of heterogeneous catalysis processes. Similarly, the future success of biorefinery is required the design of a new generation of solid catalysts for effective processing of the main components of biomass – polysaccharides and lignin.

This presentation describes the promising approaches to integrated biorefinery of wood biomass based on application of heterogeneous catalysis processes. The original results and the literature data are presented and discussed. The following scheme demonstrates an example of integrated biorefinery of lignocellulosic biomass into valuable products:



The studied integrated processing of wood biomass includes the steps of oxidative catalytic fractionation of wood on cellulose and low molecular mass lignin, acid-catalysed hydrolysis of cellulose to glucose, fermentation of glucose to bioethanol, thermal conversions of lignin to liquid hydrocarbons and nanoporous carbons. Besides, the obtained lignin can be used as non-toxic binding agent. For the promotion of key processes of integrated transformation of wood the different solid catalysts were used.

The rate of wood delignification by H_2O_2 in acetic acid–water medium is increased in the presence of suspended TiO_2 catalyst. Based on kinetic studies the optimal conditions of aspen-wood delignification process were selected which allow to obtain by “green” method at 100 °C and atmospheric pressure the pure cellulose (content of residual lignin less 1 % mas.) with an yield near 45 % mas. The application of catalytic fractionation of wood on cellulose and lignin allows to obtain the more pure solutions of glucose and to increase the yield of ethanol as compared to direct hydrolysis of wood.

Different mechanical and chemical treatments were used to increase the reaction ability of cellulose in acidic hydrolysis. All of them reduce the degree of cellulose crystallinity and polymerization degree. The most significant effect was observed for combined mechanical-chemical treatments.

All studied mesoporous acid catalysts (SBA-15, graphitized carbon Sibunit, thermally expanded graphite (TEG) and non-graphitized carbon from cellulose) were active in cellulose hydrolysis at 150 °C. The growth of content of acid groups and diameter of pores in catalysts increased the cellulose conversion into glucose.

The influence of sulfated ZrO_2 and $\text{ZrO}_2\text{--Al}_2\text{O}_3$ and zeolite catalysts in H-form with different silicate module on lignin conversion in ethanol and on the composition of obtained products was studied. Sulfated ZrO_2 -containing catalysts increase by 1.4–1.5 times the degree of lignin conversion and the yield of ethanol-soluble fraction with b.p. higher 180 °C. All catalysts promote the formation of 1,1-diethoxyethane – promising additive for motor fuels and also decrease significantly the concentration of phenol and benzol derivatives in this fraction as compared to non-catalytic process.

The partial catalytic gasification of wood, cellulose and lignin in molten KOH and NaOH makes possible to obtain nanoporous carbon with the surface area 1350–2050 m^2/g , pore volume to 1.5 cm^3/g and pore size 2.0–2.5 nm. Acid-modified active carbons and bifunctional catalysts on their basis have prospects to use in conversions of plant polymers to valuable products.

The integrated biorefinery including the stages of wood biomass fractionation on cellulose and lignin, cellulose hydrolysis and lignin depolymerization over solid catalysts allows to obtain by green way cellulose, ethanol, liquid hydrocarbons, binding agents and microporous carbons.

Acknowledgement

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Heterogeneously-Catalyzed Conversion of Biomass-Derived Carbohydrates to Chemicals and Fuels

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Lignocellulose biomass is the most abundant type of biomass and therefore the most attractive and promising renewable carbon-containing feedstock for the bio-based industry [1-4]. Wood wastes, solid agricultural wastes (cobs, sunflower husks, etc.) and high-productive crops, such as miscanthus and girasol are non-food lignocellulosic materials having a similar chemical composition. The main their components are polysaccharides (cellulose, hemicelluloses) and lignin, which are biological polymers insoluble or slightly soluble in water and other solvents. Therefore, traditional approaches to chemical processing of such materials through the use of solid catalysts are inappropriate. Hence, the main problem and the key stage of primary processing of lignocellulosic raw materials is the transformation polymers into a water-soluble form using depolymerization. As a result of depolymerization (or combination of hydrolysis and dehydration) of the cellulose it is possible to obtain such valuable chemicals as glucose, 5-hydroxymethylfurfural (5-HMF) and levulinic acid. The hydrolysis of hemicelluloses gives aldopentoses and aldohexoses which can be converted by dehydration into furfural and 5-hydroxymethylfurfural, respectively. In recent years, these compounds are called “platform molecules” for the production of components of alternative fuels and chemical feedstock.

One of the most promising approaches to solution of the problems of depolymerization of polysaccharides biopolymers is the development of solid acid catalysts which have macro- and mesoporous morphology and high stability in hot aqueous media. Such catalysts based on mesoporous graphite-like carbon material of Sibunit family and macroporous zirconium oxide (ZrO_2) were developed in Boreskov Institute of Catalysis SB RAS.

Carbon catalysts were prepared by sulfonation of mesoporous graphite-like carbon material Sibunit-4 under different temperature (80-250 °C). Catalysts were washed, treated at the hydrothermal conditions, characterized by N_2 adsorption, acid-base titration and tested in

cellulose powder hydrolysis. Application of the best carbon catalysts (sulfonated at 200 and 250 °C) produces glucose with yield up to 50 mol % and 5-HMF with yield up to 25 mol %. NbO_x/ZrO₂ catalysts with different amount of Nb (1-7 wt.%) were prepared based on macroporous ZrO₂ by the method of wet impregnation followed by calcination. Stability of the catalysts under hydrothermal conditions was tested and proved. Fresh catalysts and catalysts after hydrotreatment were characterized by XRD, XRF, SEM, N₂ adsorption. The testing of catalysts in cellulose oxidation showed high activity of 7%Nb/ZrO₂ sample. 5-HMF (yield ca. 20 mol %) was obtained over the best catalysts. The most important advantage of solid catalysts in comparison with soluble (mineral acid) catalysts is high selectivity toward to 5-HMF without appreciable formation of levulinic acid.

Moreover the solid catalysts except of the acid catalytic sites may contain also redox centers such as transition metals (Ru, Ni, Mo, W, Pt, etc), carbides, etc. The use of such catalysts allows not only performing the processes of hydrolysis of the polysaccharides but also realizing so-called “one-pot” processes combining the hydrolysis with other transformations of the derived monosaccharides into other platform molecules. For example, hydrolytic hydration of cellulose pulp at a relatively low temperature (190 °C) in a single step allows obtaining valuable sorbitol and mannitol [5]. At higher temperature (300 °C) of the cellulose the important monomers for the petrochemical industry (ethylene and propylene glycols) can be obtained with high yields [6].

This research was supported by the RFBR (Grants Nos. 11-03-01022-a, 12-03-93116-a), IP SB RAS-NAS Belarus No. 24 and Federal Special Program Scientific and Educational Cadres of Innovative Russia.

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Photo Catalysis for Waste Water Treatment and Environmental Pollution Control

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Heterogeneous photocatalysis, one of the Advanced Oxidation Processes (AOPs), has been utilized to remove a wide range of pollutants in liquid and gas phase over the past several decades. TiO₂ is one of the widely studied for the photocatalytic degradation of organic substrates due to its low-cost, non-toxic, photochemical stability and also, its appropriate energetic separation between the VB and CB (+3.1 and -0.1 eV). This degradation process is based on the formation of nonselective and highly reactive radicals (i.e. hydroxyl radicals ([•]OH) and superoxide radical anions (O₂^{•-}), as initiators of the oxidative degradation.

Research efforts have been directed towards modifications of semiconductor surfaces by addition of metals, dopants, or combinations with other semiconductors that can be beneficial in decreasing the e⁻-h⁺ pair recombination rate and thereby increasing the quantum yield of the photocatalytic process. Some of these modifications include surface chelation and covalent attachment, co-deposition and doping of metals, and photocatalysts mixtures, i.e., coupled semiconductor.

The recovery of photocatalyst after the reaction from the suspension is a very important aspect to make the catalyst reusable and the photocatalytic process cost effective. Another very important thing need to be considered is fine TiO₂ particles of high surface area to achieve the maximum output in the practical application. These can be acquired by fixing or immobilization of TiO₂ particles on high surface supporting material such as zeolites. Present talk will focus on the studies done by authors on the following aspects of photo catalysis.

- TiO₂ coated fly ash cenosphere potential material for photodegradation of oil spillage
- Ceramic surface coated photocatalyst for improving kitchen hygiene
- Effect of nanocrystalline and zeolite supported TiO₂ on its photocatalytical activity
- Effect of anions on the photocatalytic degradation of TiO₂
- Photocatalytic activity of transition metal exchanged ETS zeolites

Vibrational Spectroscopy of Surfaces for the Solution of Environmental Problems

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The lecture deals with the application of spectral studies of surface species or reactions in heterogeneous systems for the ecologically important processes in the nature, technology and in the everyday human activity. Pressed powder samples, films of porous ice or alkali halides can be used as a model of solid atmospheric aerosols. Measurements at variable temperatures and pressures enable us to reproduce the environmental conditions or those of technological processes and, if needed, to stabilize the intermediate products of chemical or photochemical reactions on solid surfaces.

Studies of low temperature ozone adsorption on oxide adsorbents or on icy films demonstrate different activity of solids in catalytic decomposition of O₃. Different rate of heterogeneous ozone reaction with ethene or chloroethenes should be taken into account when considering the peril of various atmospheric pollutants for the ozone layer.

Studies on the adsorption of different pollutants on water ice surface help to clarify the role of snow and atmospheric icy particles in air purification. To minimize the emission of CO, NO_x or hydrocarbons in the exhausted gases or gaseous wastes catalysts are used. Spectral methods help to understand the reaction mechanisms in order to raise the efficiency and to lower the price of the devices.

Particularly promising is the application of spectroscopy for the studies of photoprocesses in heterogeneous systems. Photoozonolysis was shown to be more effective as compared with separate action of ozone or irradiation in the presence of oxygen. This can be used to eliminate the traces of toxic pollutants in water or air purification. Much interest is paid to photoinduced superhydrophilic properties TiO₂. The mechanism of this phenomenon, already widely used for different purposes, is still not clear and needs profound spectroscopic studies for more successful application.

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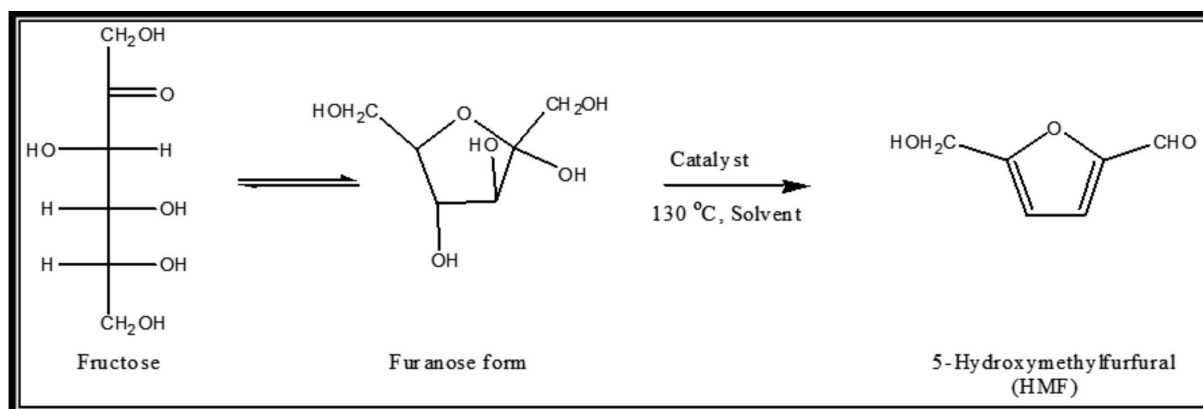
Novel Heterogeneous Catalyzed Efficient Synthesis of 5-Hydroxymethylfurfural from Carbohydrates

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Biomass has a huge potential in the production of alternative energy in the form of liquid fuels and chemicals due to the progressive depletion of conventional fossil fuels. In particular, renewable carbon resources have been the primary industrial and consumer feedstocks as fuels and chemicals. A fructose dehydration product, 5-hydroxymethylfurfural (HMF) a furfural derivative is considered as a platform chemical and key intermediate in the production of value added chemicals and fuels. Recently, many heterogeneous catalysts have been used for the conversion of carbohydrates to fine chemicals, which possess several advantages over homogeneous catalysts such as ease of separation of reactants and reusability of catalyst etc. Herein, we have demonstrated novel titania-based heterogeneous catalyst for the efficient production of 5-hydroxymethylfurfural from carbohydrates. The catalyst is thoroughly characterized by XRD, FT-IR, elemental analysis and NH₃-TPD.



The catalytic activity of the catalyst has been tested for the dehydration of fructose to HMF. The effect of solvent, salt and temperature on corresponding product was systematically investigated. Further, the catalytic activity is also tested for various other carbohydrates. The reusability results of the catalyst reveal that high yield of 5-hydroxymethylfurfural maintained for three reaction cycles.

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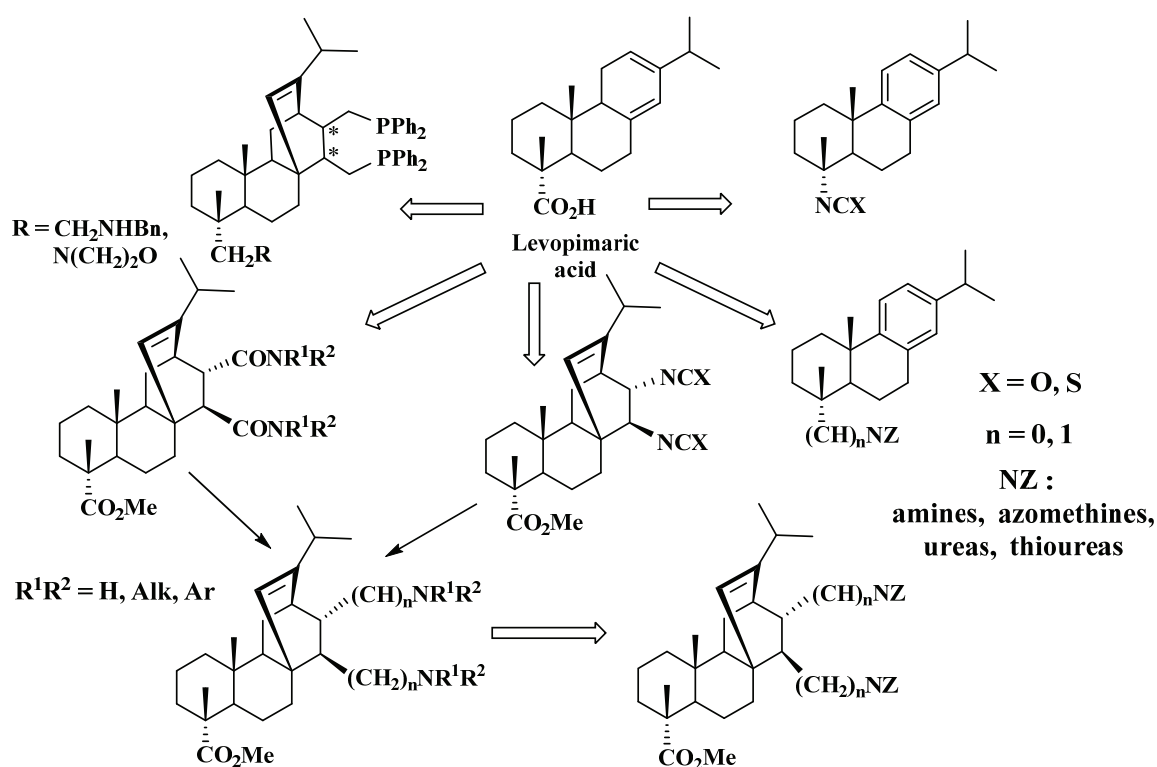
Renewable Feedstock for the Chiral Catalysts Producing

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Integrated processing of renewable natural raw materials represents an attractive alternative of the traditional petrochemical route of the synthesis of a number of practically important compounds and plays an important part in the decrease of the harmful industrial load on environment. Large-tonnage products of conifers processing - galipots and colophonies - contain numerous hydrocarbon constituents of complex structure that can serve as convenient starting materials for production of valuable chemicals with desired physicochemical properties and bioactivity, including available catalysts of asymmetric reactions, chiral reagents and materials, effective drugs and pesticides. At present resin acids constituting up to 90% of galipots and colophonies have a wide application in chemical industry, nevertheless, the whole potential of this feedstock as an available chiral pool has not been used yet. As a result of our investigation of the resin acids chemistry we have developed the efficient synthetic routes of stereoselective functionalization of optically pure available natural products – levopimaric and abietic acids.



KL-9

On the basis of stereospecific transformations of levopimaric acid adducts with fumaric acid and maleic anhydride a series of optically pure diastereoisomeric P-, N- containing terpenoids were prepared. Using the dehydroabiatic acid a series of nitrogen derivatives was synthesized. The produced optically pure tricyclic diterpene derivatives – chiral mono- and diamines, azomethines, ureas and thioureas, phosphines and phosphinites - can serve as optically pure reagents, chiral organocatalysts and P-, N- donor chiral ligands for metal complexes. Complexes of the synthesized P-, N- donor chiral ligands with Rh(I), Ru(II) and V(IV) were prepared and used as catalysts of asymmetric reactions.

The work is supported by RAS Program of basic researches, project N 5.7.3

Photocatalytic Properties of Mesoporous Titania

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Semiconductor materials are commonly used as a photocatalysts as the electrons and holes can be effectively used to split water to produce hydrogen and oxygen provided its conduction band and valance bands are suitably fixed for hydrogen and oxygen evolution potentials. In this regard, conventional bulk titania is the one of the well studied and promising materials, however, it suffers from the disadvantages of rapid recombination of photo-generated electrons and holes as well as photocorrosion. Therefore, we have focused our attention to design and develop titania-based photocatalytic materials, and identified mesoporous titania with varied crystallite and pore size characteristics as suitable for water splitting reaction (Figure 1). Further, in order to minimize the rate of recombination of electrons and holes, we have loaded nano-sized platinum on the mesoporous titania as this will allow the trapping of photo excited electron rather recombination with hole in the valance band. Likewise, to decrease the photo-corrosion problem, we have employed methanol as sacrificial agents.

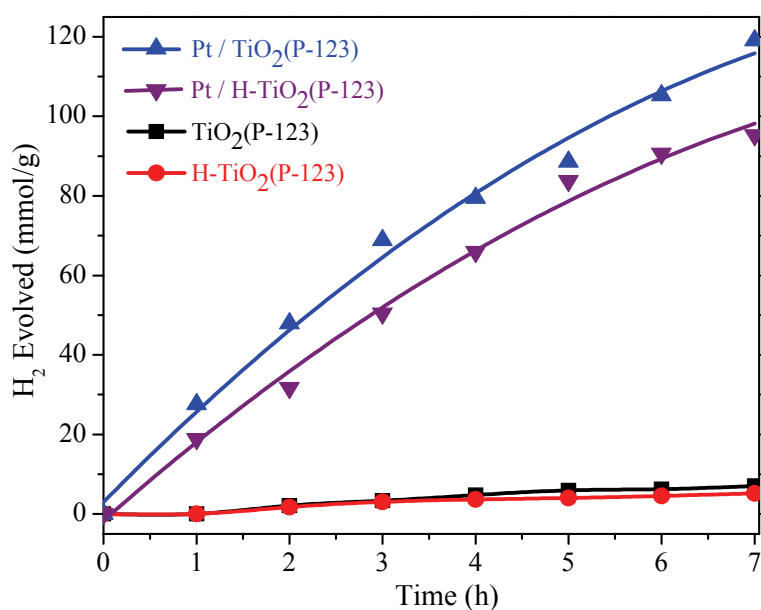


Figure 1. Photocatalytic hydrogen production over mesoporous titania [1].

KL-10

Incidentally, bulk titania is also extensively used for the photocatalytic degradation of organic compounds but the activity is greatly compromised due to low surface area. Hence, we have effectively utilized the mesostructured titania which possesses large surface area, high pore volume and huge pores and 4-chlorophenol was employed as a probe molecule to evaluate the photocatalytic activity of mesoporous titania (Figure 2).

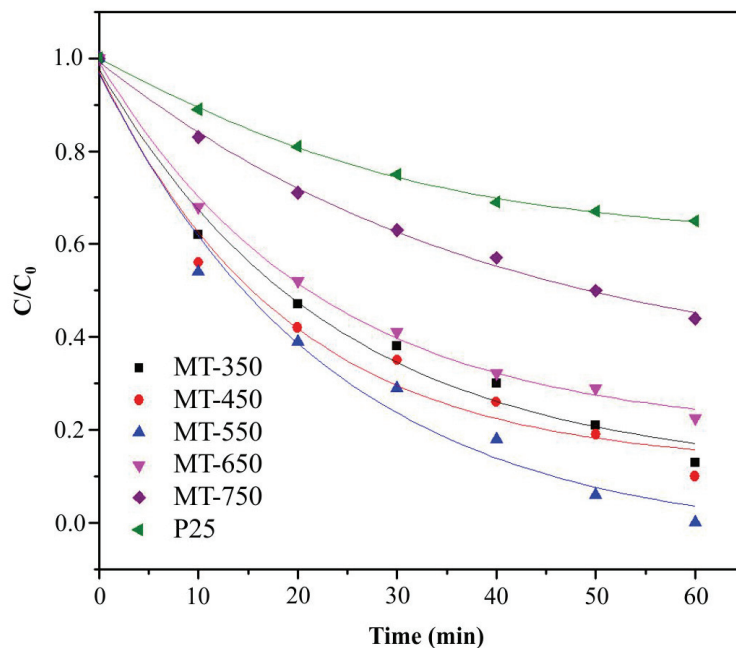


Figure 2. Photocatalytic degradation of 4-chlorophenol over mesoporous titania.

The development of such materials of well-defined geometry with precise and easily controllable pore shape and size is of great importance. In this context, the preparation of high quality materials with designed pore structures is of paramount importance for many applications in areas including catalysis, adsorption, separation and nanomaterials. In designing such materials, several characteristics such as modification of framework structure, pore size, shape and interconnectivity, etc. must be addressed. In this presentation, a brief account of the recent development on the subject will be discussed.

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Particle Size Effect in Oxidation Catalysis for Environmental Protection

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Applied oxidation catalysis is the largest area in the field of environmental catalysis covering catalytic abatement of volatile organic compounds (VOCs), CO, soot, etc. For this purposes platinum group metal (PGM) catalysts are applicable in almost every case. However, the challenges for a company producing commercial catalysts are to find the most optimal catalyst at the right price. Theretofore, the efficiency of PGM utilization becomes the primary focus from applied and fundamental viewpoint.

This lecture will highlight three aspects of oxidation catalysis by comparing Pd and Pt catalysts in CH₄ or n-C₄H₁₀ complete oxidation:

- (a) Effect of particle size on TOF (turnover frequency) and the overall activity;
- (b) Relationship between particle size effect and a support effect;
- (c) Significance of particle size effect under realistic conditions.

It will be shown that Pd and Pt catalysts demonstrate evidently different “TOF-particle size” relationships. Moreover, activities of Pt catalysts strongly depend on the support nature: Pt/TiO₂ catalysts exhibit notably higher activity than Pt/Al₂O₃, or Pt/SiO₂. On the other hand, support nature does not essentially influence activities of Pd catalysts. All these observations suggest distinctly different reaction mechanisms over Pt or Pd catalysts.

Detailed study of the reaction mechanism by combination of *in-situ* XPS and kinetic measurements suggests that the different behavior of Pt and Pd catalysts can be attributed to different reaction mechanisms. Over Pd catalysts hydrocarbon oxidation proceeds via Mars–van Krevelen mechanism, while over Pt catalysts Langmuir–Hinshelwood mechanism prevails.

From practical viewpoint, it is important to evaluate a significance of size effect under realistic conditions, e.g. under conditions of real engine exhaust. The last part of the presentation will be focused on discussing effect of water vapor and oxygen concentration of the “TOF-particle size” relationships and overall activities for the series of Pt/Al₂O₃ catalysts with different sizes of Pt particles.

Acknowledgements

We gratefully acknowledge funding for this work from the Russian Foundation for Basic Research (RFBR), grant # 12-03-01104-a and # 13-03-01003-a

The Impact of the Reaction Medium on Catalysts for Automobile Exhaust Gas Neutralization: Structure of Components and Spatial Distribution of Chemical Elements

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The work concerns the high-temperature interaction of reaction gas environment with samples of industrial and model catalysts designed for automobile exhaust neutralization. The catalysts are multicomponent systems, which include noble metals (Pt, Rh, Pd), oxide support (La-stabilized γ -Al₂O₃,) and other oxide components. The catalysts were deposited on the walls of channel in cordierite blocks. Samples of the catalysts were aged under hydrothermal conditions at 1050 °C (HTC) and in flowing exhaust gas in an engine bench. To assess the reaction medium impacts, the fresh and aged samples of the catalysts were characterized by TEM, XPS, TPR, SEM and XRD methods, as well as by measurement of the oxygen storage capacity and the catalytic activity in the processes of CO, NO_x and hydrocarbons neutralization.

The interaction with the reaction medium is found to induce the following processes changing the structure of catalysts and the spatial distribution of components within catalysts:

1. Migration of noble metals (Pt, Rh, Pd) resulting in alloying and metal transfer from one component of the support to another one, which can be accompanied by increase in the metal dispersion;
2. Changing the phase composition of the support (γ -Al₂O₃ → α -Al₂O₃);
3. Change in the spatial distribution of elements within the oxide components, such as lanthanum segregation on the surface of Al₂O₃ support and CeO₂-ZrO₂ mixed oxide;
4. Changes in the morphology of CeO₂-ZrO₂ mixed oxide particles, which are accompanied by changes in their chemical composition, e.g. the formation of cerium-rich filamentous particles with an increased concentration of Rh;
5. Transfer of elements forming the cordierite substrate to the catalyst washcoat.

The influence is discussed that these changes in the structure and spatial distribution of components exerts on the catalytic activity.

Renewable Wastes (Rice Husk Ash, Acid Oil, CNSL etc) as Raw Materials for Industrially Important Value Added Products

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The renewable raw materials for the production of fuels and chemicals are the main drivers for sustainable development and growth without adversely effecting our environment. However, the availability of desired or suitable biomass at affordable price is also a big issue. Hence, the waste generated from biomass processing like agri-waste or waste of vegetable oil refining process become important raw materials.

In this context we present our work done in the area of developing various value added chemicals as mentioned below:

- Low cost water purifier using Rice husk ash and Ag nanoparticles.
- Lignocellulosic waste biomass (sugar cane bagasse) to Xylose and xylitole.
- Acid oil to high value esters for skin care and functional foods using proprietary solid catalysts.
- Anacardic acid from waste CNSL (Cashew Nut Shell Oil) for cosmetic applications.



ORAL PRESENTATIONS

OP-1 ÷ OP-6

OS-1 ÷ OS-8

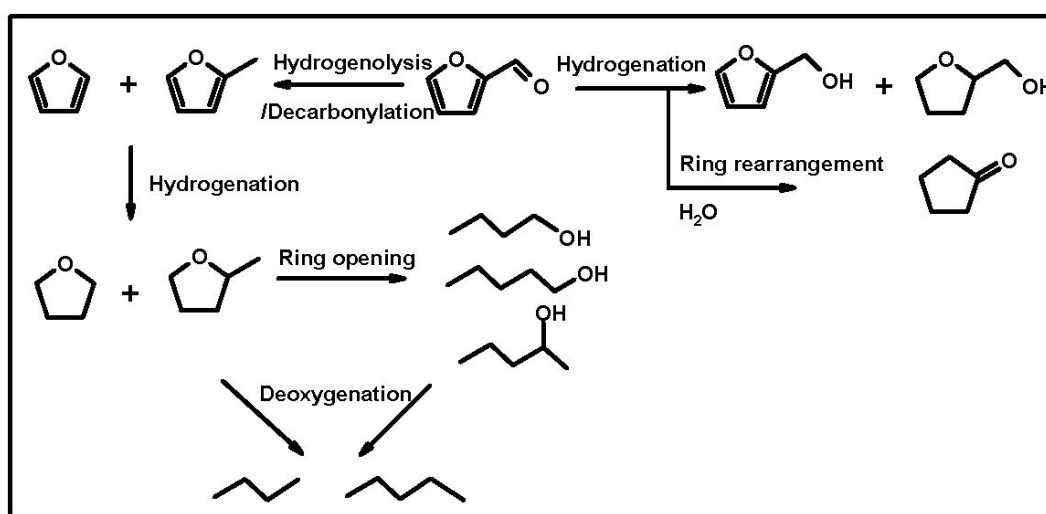
Selective Hydrogenation and Hydrogenolysis of Furfural to Industrial Chemicals over Supported Group VIII Metal Catalysts

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At present, a majority of industrial chemicals are manufactured from petroleum feedstocks. In view of depleting fossil fuel resources, there is need to develop sustainable chemical processes based on renewable feedstocks. Lignocellulosic biomass is available in good quantities at affordable price. World-wide, considerable attention is being paid to convert lignocellulose into platform chemicals viz., sugars, lignin and furan derivatives. Furfural is an important chemical derived from C5 sugars viz., xylose and arabinose. Selective hydrogenolysis / hydrogenation of furfural yields a variety of industrial chemicals including furfuryl alcohol, tetrahydrofurfuryl alcohol, methyl furan, furan, tetrahydrofuran, pentane diol and butanol. Over hydrogenation/hydrogenolysis can lead to butanes (Scheme 1). Development of solid catalysts for selective conversion of furfural or C6 sugars-derived hydroxymethyl furfural (HMF) to value-added chemicals is a challenging task. Quite often, the catalyst is unstable and cannot be reused in recycling experiments of biomass. With a view to understand the chemistry of hydrogenolysis/hydrogenation and to develop stable solid catalysts, we report here, the applications of supported Gr. VIII catalysts for transformation of furfural to various chemicals. The influence of support, metal and reaction parameters on product selectivity will be discussed.



Scheme 1. Catalytic pathways for conversion of furfural to chemicals

Aromatics from Bio-Mass Based Furan Derivatives

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Fossil resources supply most of the today's demand of energy and chemicals, however, depleting petroleum sources is unlikely to meet the growing needs of humanity. Renewable sources based feedstocks are thought to provide atleast partly, potential solution especially with the growing concerns about global warming and sustainability in the near future. Biomass such as agricultural wastes, forest woods, energy crops, aquatic biomass etc could be potential feedstock to produce variety of chemicals [1]. Among chemicals, aromatics are of great interests for their wide range of applications and currently naphtha from petroleum sources is the main source of aromatics.

Several studies have been reported for the conversion of especially lignocellulosic biomass to aromatics including benzene, toluene, and xylenes (BTX) through pyrolysis in the presence of a zeolite catalyst [2,3]. However, selectivity to aromatic compounds are relatively low due to other byproducts such as a olefins CO, CO₂, H₂O along with decent quantity of coke[4]. Thus, obtaining aromatics with high selectivity has been the key challenge.

Furanic compounds via 5-hydroxymethylfurfural, 2,5-dimethylfuran, 2-methyl furan produced from cellulose and other carbohydrates using relatively simple processes, can be a potential source for BTX with high selectivity. High selectivity is typically achieved in the presence of co-feed which is hydrogen-rich hydrocarbons such as olefins. Studies with ethylene and propylene co-feeds furan derivatives showed improved aromatics yield especially for BTX, and with smaller amount of styrene, indene, and naphthalene. The chemistry can be tuned more specifically to produce *p*-xylene, terephthalic acid precursor, to make polyethylene terephthalate, if olefins are co-feed with 2,5-dimethylfuran with a suitable catalyst [5].

Recent developments on the aromatics production from the furan derivatives obtained from biomass will be discussed in detail.

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Catalytic Conversion of Biomass: Role of Catalyst Properties

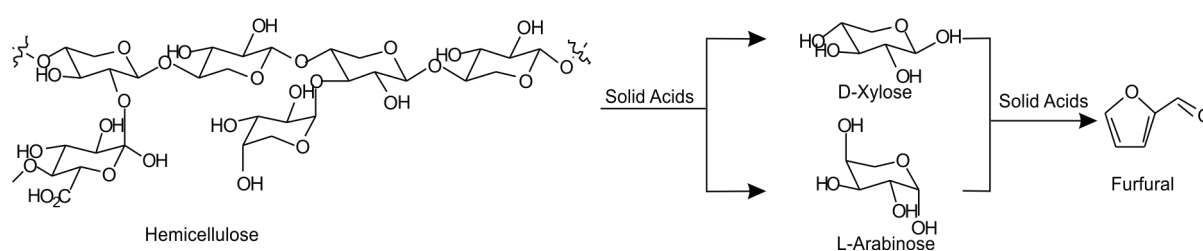
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Lignocellulosics, a plant derived non-edible biomass is made up of cellulose (40-55%), hemicelluloses (20-35%) and lignin (12-25%). Until now homogeneous acids and enzymes are used to convert starch, cellulose and hemicellulose into chemicals.^{1,2} However, it was also shown that heterogeneous catalysts could ably convert cellulose.³ Our group has for the first time shown that selectively hemicelluloses, a polysaccharide made up of mainly C5 sugars can be converted to C5 sugars and furfural directly from real substrate (lignocellulosics, without separation of cellulose, hemicelluloses and lignin) using solid acid catalysts such as, clays and zeolites.⁴ It has been also observed that lignin, an aromatic polymer can also be converted to aromatic monomers using solid acid catalysts. However, detailed characterization of the spent catalysts revealed that zeolites undergo structural changes.⁵ Hence the objective of the work was to synthesize the stable catalysts.

For the conversion of hemicelluloses (scheme 1) acid catalysts such as tungsten, gallium or molybdenum incorporated in silica are synthesized either by impregnation or sol-gel method. The catalysts were calcined at 500-800°C.



Scheme 1.: Hydrolysis of hemicellulose using solid acids.

In a typical reaction, hemicellulose, solid acid catalyst, and solvent were charged in an autoclave and the reactions were performed at 130-170°C for desired time. The tungsten-silica and gallium-silica catalysts gave ca. 36% furfural yield after 6 h with ca. 90% conversion. Though molybdenum catalyst showed less activity than other catalysts but still it was active. The prepared catalysts showed activity less than the structured catalysts such as zeolites (Figure 1) however, the catalysts showed similar activity up to 6 recycles.

OP-3

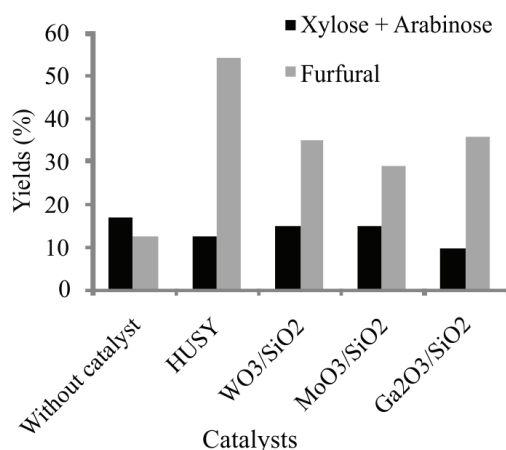


Fig. 1.: conversion of hemicellulose into C5 sugars and furfural. 170 °C, 6 h, N₂20 bar

Conversion of hemicellulose and lignin using other solid acid catalysts is also carried out and we have found few of the stable catalysts. The catalysts are characterized with XRD, TPD-NH₃, and ICP. More discussions will be done during the presentation.

Besides above mentioned catalysts hydrothermally stable silicoaluminophosphate catalysts were synthesized and used in the reactions. It was observed that based on the substrate and reaction conditions catalysts morphology changes.

In lignin conversions ca. 60% yield for aromatic monomers was obtained using solid acid catalysts. The catalysts stability depends on the type of lignin used in the reaction.

The details on the catalyst property-catalytic activity correlation will be discussed during presentation.

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Drop-in Biofuels and Chemicals Produced by Hydroprocessing of Lipids

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Jet fuels must meet very stringent international specifications, due to which it is much more difficult to develop an alternative fuel for aviation than for automobile applications.¹ Drop-in type biofuels for aviation (biojet) are in high demand for several reasons. Firstly, they provide security to the Airlines against fluctuation in ATF prices; secondly, ATF availability is expected to reduce gradually in the future; additionally, they have lower carbon footprint. The ASTM committee has now approved up to 50 % blend of biojet fuels with normal fuels (ASTM D7566).

CSIR-IIP has taken a step forward for the development of aviation fuel from non-edible oil (such as Jatropha). Hydroprocessing Lab of CSIR-IIP has developed catalyst and process for the conversion of plant oils directly to aviation fuel (drop-in type fuel). CSIR-IIP is the first institute in India to produce 150 liters of high quality biojet fuel from jatropha curcus oil for aircraft engine manufacturer Pratt & Whitney, Canada. This fuel has been tested by both Indian Oil Corporation and HPCL and has been found to meet all specifications as per ASTM D 1655 and ASTM D7566 for Jet A-1 fuel (ATF). A large pilot plant with 20 litre per day production of Bio-Jet is in operation, which is producing enough fuel for testing in aircraft engines.

Hydroprocessing catalysts supported on mesoporous zeolites, silica-alumina and alumina supports were used to convert triglycerides to obtain pure hydrocarbons, from jatropha oil. The desired products were obtained when using



OP-4

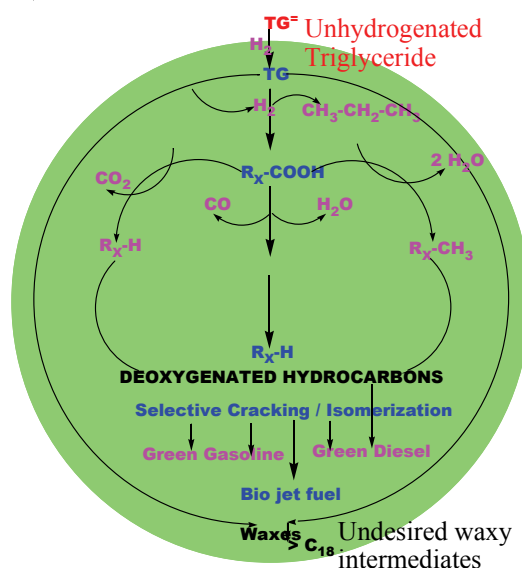
highly acidic supports in a single step. But, the long-chain hydrocarbons produced from hydrotreating reactions (over alumina supported catalyst) can also be selectively hydrocracked and hydroisomerized in the second step using suitably designed catalysts to give products that include jet fuel range hydrocarbons. The entire process involves pre-treatment of plant-oil followed by hydrodeoxygenation, hydrocracking, hydroisomerization and aromatization. Hydro-conversion reactions were carried out in fixed bed trickle reactor with sulfided catalysts. The process is very similar to refinery processes hence it can also be integrated to the current refinery infrastructure.² Several patents have been filed for this invention.³ The product hydrocarbon mixture is distilled into gasoline, kerosene (jet fuel) and diesel range products. About 40% of the product is kerosene which meets jet fuel specifications, another 40% can meet the diesel specifications.

The engine evaluation emission results showed 9% reduction in NO_x, 10% reduction in particulate matter (PM), and 2% reduction in fuel consumption with renewable diesel produced by hydroprocessing route compared to conventional diesel. The improved performances of renewable diesel than conventional diesel may be attributed to lower (poly)aromatics, lower sulfur and lower nitrogen content in the former.

The catalytic process has the potential to manufacture petrochemical (aromatics rich) feedstock pool along with hydrocarbon based by processing the lipids, over a hydroprocessing catalyst.

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Scheme 1: General representation of processing of triglycerides

New Approach to the Stabilization of Bimetallic Three-Way Catalysts for Exhaust Gas Purification

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In the last decades, the ever increasing interest in automotive catalysis is mainly caused by the toughening of the vehicle emission regulations that makes it urgent to develop more effective and reliable but less expensive catalytic systems. The three-way catalysts (TWC) are used in internal combustion engines for simultaneous conversion of unburned hydrocarbons, carbon monoxide (CO) and nitrogen oxides (NO_x) [1].

Bimetal alloy systems have been recently proposed for TWC applications. The catalytic properties of alloys are known not to be additive activities of individual components. For example, the 15 nm bimetal Rh_{1-x}Pd_x nanocrystals were shown to exhibit significant synergistic effects during CO oxidation [2]. The observed synergism is caused by preferable adsorption of CO on isolated Pd atoms, or on the islands at the metal surface and spillover of the adsorbed oxygen from rhodium to palladium centers covered by adsorbed CO.

The present study was focused on the activity and stability of bimetal alloy Pd-Rh catalysts obtained from heterometal complexes and supported on γ -Al₂O₃. Conventional catalytic systems contain more than 2 % of active components. Nevertheless, the much lower contents of precious metals are interesting for practical application. The catalysts with low content (0.2 %) of precious metals were prepared and studied. Studies of the catalytic activity and stability of alloyed Pd-Rh catalysts revealed that these are systems competitive in performance with the commercial catalysts. The stability of the bimetal Pd-Rh alloy catalysts is superior to monometal and mechanically mixed samples with identical metal concentrations. Studies of the catalyst stability and testing the catalysts in ethane hydrogenolysis showed that the decomposition of the dual complex salts on the support surface produced particles of rhodium and palladium oxides. The bimetal alloy was formed on contact with the reaction medium. Photoluminescence spectroscopy showed that the bulk diffusion of rhodium can be minimized due to the formation of stable rhodium and palladium

OP-5

alloy particles on the support surface. With the catalyst prepared by mechanical mixing, rhodium diffuses rapidly at elevated temperatures and ultimately gets encapsulated into the corundum phase.

Financial support from Russian Foundation for Basic Research (grant #13-03-00988) is gratefully acknowledged.

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Engineered Materials for Environmental and Energy Related Applications

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Energy and environmental issues in a global level are important themes to be tackled in 21st century. Some of the key research areas include, photocatalytic hydrogen generation with recourse to waste treatment and carbon capture valorization and sequestration (CCVS) for cleaner air and energy resources. In order to meet the challenges of these research areas a new and different approach of engineering natural processes is being pursued in our group. Accordingly, new advanced materials with improved properties are being designed and developed by bio-mimicking the natural processes for tackling pollutants like CO₂, preferably, in Nature's way. Prior to industrialisation, CO₂ in the atmosphere was being stabilized by natural processes like photosynthesis, humification, carbonation etc. However, with alarming increase in the level of CO₂ the natural processes are unable to control the levels of CO₂ and therefore it is required to biomimic the natural processes and re-engineer materials to control the growing levels in a cleaner, greener and sustainable manner. Thus several environmental and energy technologies are envisaged with substantial benefits from new and re-engineered materials and processes using tools of biocatalysis, photocatalysis and biophotocatalysis singly or in combination. The important areas thus being investigated at CSIR-NEERI are 1) Plasmonic and functional nanomaterials for photocatalytic generation of hydrogen using model pollutants and 2) Immobilised and stabilised enzyme for biomimetic carbon capture, sequestration and valorisation (CCVS) with specific reference to generation of syngas and other value added products.

1) Plasmonic and functional nanomaterials for photocatalytic generation of hydrogen

Plasmonic photocatalysts are showing a significant edge over the conventional photocatalysts in terms of their visible light absorption properties. 1- 5 wt% of Au and TiO₂, CeO₂, Cu₂O and Fe₃O₄ composites have been synthesised via the photo deposition method to illustrate the influence of SPR (Surface Plasmon Resonance) on photocatalytic hydrogen generation. Au/TiO₂ shows hydrogen evolution rate of 920 μmol h⁻¹ and 32.4 μmol h⁻¹ under UV-visible and visible radiation, respectively followed by Au/CeO₂, Au/Cu₂O and Au/Fe₃O₄ for SED (Sacrificial Electron Donor) assisted water splitting under UV-vis radiation.

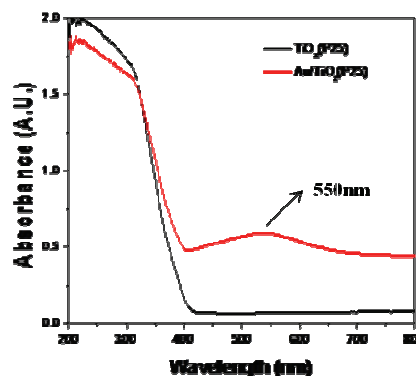
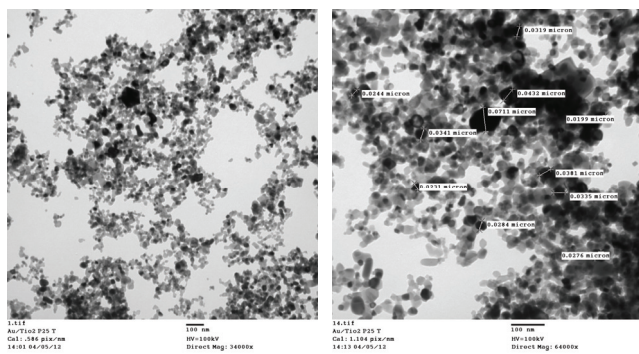


Fig 1: TEM images of Au /TiO₂ composites **Fig 2: UV DRS of Au/TiO₂ composites**

Biomimetic materials for solar hydrogen: In-situ nanostructured Titania and other plasmonic photocatalysts have been developed using algae as ‘nanoreactor’. The photocatalyst shows exceptionally high hydrogen evolution to the tune of about 17.50 mmoles/h/g of photocatalyst (sensitized algae) as compared to 0.0906 mmoles/h/g of photocatalyst (algae as such) establishing its superior photocatalytic activity especially in the visible light region under solar energy irradiation.

2) Immobilised and stabilised enzyme nanoparticles for biomimetic carbon capture, sequestration and valorisation (CCVS): Efforts are being made worldwide to mimic the reaction for fixation of anthropogenic CO₂ into calcium carbonate using carbonic anhydrase (CA) as a biocatalyst. CA has been immobilised on different matrices and tested for reuse and recyclability. Also a unique protocol for the synthesis of stabilized enzyme nanoparticles (SENs) has been developed for carbonic anhydrase to stabilize the enzyme activity by encapsulating each enzyme molecule with a hybrid organic/inorganic polymer network. The K_m and V_{max} of free SEN is 6.143 mM and 0.02857 mmole/min/mg as compared to K_m and V_{max} of 1.252 mM and 0.02029 mmole/min/mg respectively for free enzyme. CA is being employed to accelerate the rate of hydration of CO₂ to form carbonate ions and proton. Efforts are being made to couple biomimetic carbonation with photocatalysis to generate high value added products including formic acid, hydrogen, syngas etc. This approach may prove to be a revolutionary technical advancement required for hydrogen economy demanding carbon neutral hydrogen production.

Engineered materials and processes ensures cleaner and greener and sustainable environment.

Mesoporous Molecular Sieves as Catalyst for Selective Oxidation of Lignin Model Guaiacyl Units to Fine Chemicals

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The ever increasing carbon demand and depleting petroleum resources have urged the researchers to focus on converting waste into wealth. The search for suitable transformations of bio-based waste into meaningful applications has been the attention as the biomass is inherently green, renewable and widely abundant. Among the different constituents of biomass, lignin plays a vital role being the most abundant resource of aromatics. The structure of lignin suggests that it can possibly be fragmented into smaller valuable aromatics. However, it's a challenge to chop the highly intricate structure of lignin in a systematic manner. In this regard, an optimistic report by Bozell et al. [1] have envisaged that catalysis will be the key technology both in the area of degradation of lignin as well as finding useful application of lignin residues.

The present discussion involves some of our results which we have obtained over last couple of years, essentially focused on development/screening of a series of mesoporous catalyst for the oxidation reactions of lignin model guaiacyl units. Mesoporous catalysts studied were pristine SBA-15, MCM-41, HMS and modified catalysts were SBA-15 containing cobalt as the active species, i.e., either as cobalt inserted during synthesis or as salen complexes. Lignin model guaiacyl units [2], the monomer [1-(4-hydroxy-3-methoxyphenoxy)-ethanol, *apocynol*] and dimer [1-(4-hydroxy-3-methoxyphenoxy)-2-(2-methoxyphenoxy)-propane-1,3-diol] were investigated as representative molecules. Reactions were performed both under conventional heating as well as using microwave irradiation, in liquid phase and hydrogen peroxide as the oxidant.

Mesoporous silica catalysts resulted in unprecedented activity towards oxidation of apocynol, resulting in high substrate conversion and appreciable yield of acetovanillone and methoxybenzoquinone [3]. On the other hand, Co(salen)/SBA-15 showed high substrate conversion towards apocynol oxidation and selective towards 2-methoxybenzoquinone. Interestingly, guaiacyl-glycerol- β guaiacyl-ether produced 2-methoxyphenols over Co(salen)/SBA-15 catalyst, under microwave activation [4]. Recently, we have studied the

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reactions of apocynol over CoSBA-15 catalyst in liquid phase at ambient conditions. Under very mild conditions we have achieved complete conversion of the substrate along with appreciable 2-methoxybenzoquinone yield and very high selectivity [5]. Further, the recyclability experiments were conducted to verify the heterogeneous nature of the catalyst.

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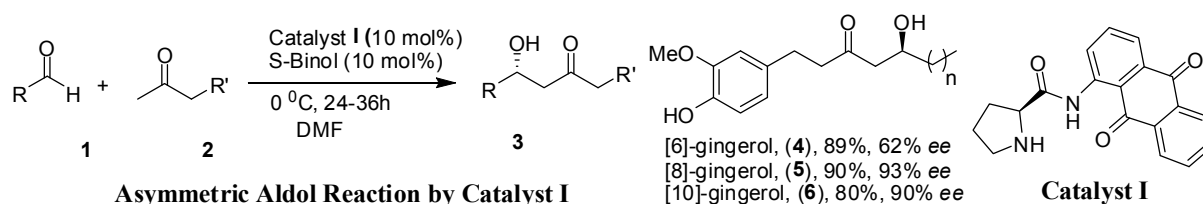
N-(1-Anthraquinone)prolin-2-carboxamide as an Efficient Organocatalyst for Novel Asymmetric Organic Transformations

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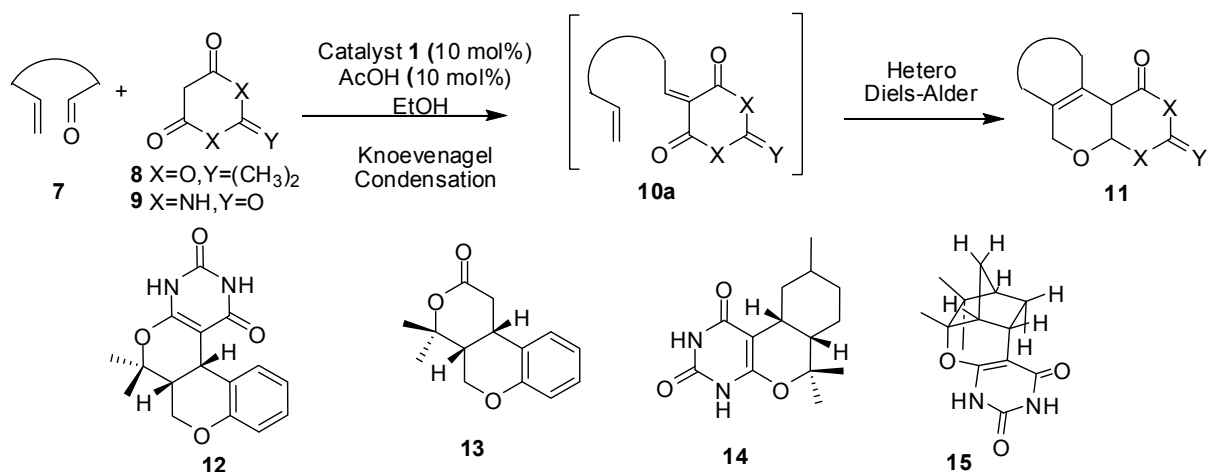
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Chiral organocatalysts, metal-free small molecules, has emerged as a highly efficient synthetic tool in enantioselective organic transformations.¹ Organocatalysts are generally nontoxic, stable to moisture and air, recovered and reused, fairly easy to design and synthesize from readily available chiral sources, and in many cases allow reactions under mild conditions. Most importantly, it can reduce the 'E' factor very significantly. An important event in the history of asymmetric organocatalytic reaction was the discovery of efficient L-proline-mediated asymmetric Robinson annulations.² Since then a wide range of small organic molecules mainly proline and prolineamide derivatives have been shown to be efficient catalysts for a series of asymmetric organic reactions. The amide derivatives of proline act as catalyst mainly through covalent interactions such as enamine or iminium catalysis. The presence of chiral template with or without sites for intermolecular interactions or a bulky environment provides enhanced selectivity.



Aldol reaction, which can generate β-hydroxy ketone functionality in one step, has been extensively used as a key step in the synthesis of several natural products. However, the main drawback associated with the aldol reaction is the self condensation of aldehyde instead of the cross-aldol reaction. In domino-Knoevenagel-hetero-Diels-Alder (DKHDA) reaction, sequential transformations takes place to give rise to annulated dihydropyrans and other heterocycles. More interestingly this can produce two or more chiral centres and give rise to some complex chiral molecules in a single step.

OS-2



Domino Knoevenagel-Hetero-Diels-Alder Reaction by catalyst I

As a part of our effort to develop green catalysts for organic transformations a novel prolineamide derivative, N-(1-anthraquinone) prolin-2-carboxamide, was prepared and its synthetic utility, as an organocatalyst, was demonstrated in asymmetric aldol reaction and DKHDA reaction. A shortest asymmetric synthesis of gingerol was achieved and some complex hetrocyclic systems were synthesised. All the products were obtained in high yield and good optical purity. The optical purity of the products was determined using the chiral HPLC.

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Cu/ZSM-5 Catalysts for the Deep Oxidation of Organic Ecotoxicants in Aqueous Solutions by H₂O₂. Structure of Active Centre and Reaction Kinetics

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Catalytic wet peroxide oxidation (CWPO) is ecologically attractive catalytic process aimed to deep oxidation of toxic weakly biodegradable organic [1,2]. There are a number of publications on CWPO of organic substrates over Fe/ZSM-5 zeolites [2-5]. Much less information on the catalytic properties of Cu-containing zeolites is available [2,6]. Here, we are reporting our systematic study of Cu/ZSM-5 catalysts in CWPO of various organic pollutants.

The catalyst samples were prepared by ion exchange (IE) from the protonic form of ZSM-5. We varied the Si/Al ration and Cu content (0.3 – 3 wt.%) in catalyst composition. The prepared catalysts were characterized by ICP, EPR, XRD, UV-Vis and tested in CWPO of formic acid using a batch reactor. Copper state in the spent catalysts was studied by EPR, UV-Vis. Contents of hydrogen peroxide and organic substrate was analyzed in the course of the reaction by sampling from the reaction solution.

The algorithm using the stable numerical method for the integration of reaction rate to give the estimated function of the concentration with the time was applied for analysis of the experimental kinetics data. Screening of catalytic properties of Cu-containing zeolites in CWPO of model organic substrates has shown that Cu-containing zeolites ZSM-5 with the atomic ratio Si/Al equal 30 and the content of Cu from 0.5 to 1 % prepared by ionic exchange and capillary impregnation are the most promising. The leaching of copper from these catalysts during the process does not exceed 3-5 %.

OS-3

The study of the electronic state of Cu-ions in initial catalysts and catalysts after reactions allows us to make the following assumption. The high efficiency Cu/ZSM-5 is provided by structured oxide clusters of copper localized in the channels of zeolite. These structures seem to be formed also of isolated Cu^{2+} ions released from the zeolite framework in the course of the reactions. The formation of copper structured oxide clusters in regular channels of zeolite with the size of 0.54-0.56 nm provides high activity in CWPO. In acidic reaction media due to easy transitions of Cu^{2+} to Cu^+ in close located cations of copper and to high stability. The formation of large oxide clusters of copper on the surface of zeolite crystallites leads to low activity and to leaching of copper in acidic media.

The influence of temperature on the rate of oxidation of formic acid and phenol in the presence of 0.5% Cu/ZSM-5-30 was studied at 30, 50 and 70 °C. The oxidation rate increased with elevation of temperature. The influence of the substrate and oxidant concentrations on the reaction kinetics was studied experimentally by varying the initial substrate concentration at a constant inlet concentration of hydrogen peroxide or by varying the oxidant concentration at a constant concentration of substrates. Different weighed samples were used at identical initial concentrations of substrate and hydrogen peroxide for determining the reaction order in respect of the catalyst. Several kinetic models were tested for kinetic analysis. Suggested models good fit for both substrates was achieved with kinetic equation with variable order of the reaction rate on the concentrations. In the case of phenol, suggested model allows to explain a low order of the reaction rate on the hydrogen peroxide, and the negative order on the substrate.

Thus, the high efficiency Cu/ZSM-5 is provided by structured oxide clusters of copper localized in the channels of zeolite. Numeric analysis allowed to choose the best kinetic models for both substrates.

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Synthesis and Investigation Pt/SO₄²⁻/ZrO₂ System Supported on Al₂O₃ in n-Hexane Isomerization

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Due to restrictions on the content of aromatic hydrocarbon in gasoline and the gradual banning of MTBE, isomerization of short paraffins (C₅-C₆) has become a process of growing popularity as a supplier of octane points for the gasoline pool. The skeletal isomerization of short paraffins is catalyzed by solid materials of strong acidity, for example sulfated zirconia (SZ). To reduce costs, improve surface properties, and find a mechanically stable form of sulfated zirconia suitable for large-scale industrial processes, the possibility of supporting SZ should be studied. Common supports for SZ found in literature are SiO₂, γ -Al₂O₃ and the zeolite.

The purpose of my work is to examine the effect of synthesis parameters Pt/SO₄/ZrO₂ systems supported on SiO₂ and Al₂O₃ on their activity in the isomerization reaction of n-hexane.

Supported SZ catalysts were prepared by varying such factors as the ZrO₂ precursor, the number of impregnation of solution of Zr(SO₄)₂, the nature of support and calcinations conditions.

The catalysts were prepared by impregnation of support SiO₂ and Al₂O₃ with an aqueous solution of Zr(SO₄)₂·4H₂O. The samples were then dried at 120°C followed by re-impregnation of solution and calcinations at 600-750°C, and subsequently impregnated with the H₂PtCl₆ using the incipient wetness technique. The solids were dried at 120°C before the final calcinations in flowing air at 450°C for 1 h.

The resulting catalysts were investigated by a low-temperature nitrogen adsorption, XRD, IR spectroscopy of adsorbed CO, TEM, and tested in the isomerization reaction of n-hexane. Isomerization of n-hexane was carried in flow reactor at H₂ pressure 1.5MPa in temperature range 140-220°C.

Study the influence of calcinations temperature had showed that the crystalline phase of ZrO₂ is formed only during calcinations at 750°C. The XRD patterns show that the catalysts supported on SiO₂ was formed as a mixture of monoclinic and tetragonal ZrO₂, but the

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catalysts supported on Al_2O_3 was formed as tetragonal ZrO_2 . Catalysts supported on Al_2O_3 were more active than catalysts supported on SiO_2 in the reaction of isomerization.

Amount of impregnation has significant effect on the structural and catalytic properties of catalysts SZ supported on Al_2O_3 . The most important changes occur in the phase composition and acid properties. XRD showed that aluminum sulphate appears in the samples supported on alumina by twice treatment ($\text{Pt/SZ/Al}_2\text{O}_3$ -2). IR spectroscopy showed that the part of strongest acid sites characteristic for zirconium oxide increases. These results explain the significant change in the activity of the twice treatment catalyst compared with first treatment catalyst. The yield of hexane isomers have achieved 75% in twice treatment catalyst in the temperature range 160-200°C, which is close to the activity of a bulk SZ (fig.1).

Pt plays an important role in the composition of the SZ catalysts. Catalysts without Pt quickly deactivated. One of the proposed roles of Pt is to prevent coke formation and increase the stability of the SZ catalyst. According to the TEM the $\text{Pt/SZ/Al}_2\text{O}_3$ -2 contains the tetragonal ZrO_2 and $\gamma\text{-Al}_2\text{O}_3$. The Pt located on the $\gamma\text{-Al}_2\text{O}_3$ in the form dispersed particles of size 1-3 nm (fig. 2).

Thus, it is possible to establish that

1. A solution of $\text{Zr}(\text{SO}_4)_2$ act as a sulfate agent at impregnation of alumina.
2. Repeated treatment alumina increases the size of the crystallites of the tetragonal phase of ZrO_2 and acidic properties, which leads to increase the yield of hexane isomers in the temperature range 160-200°C.

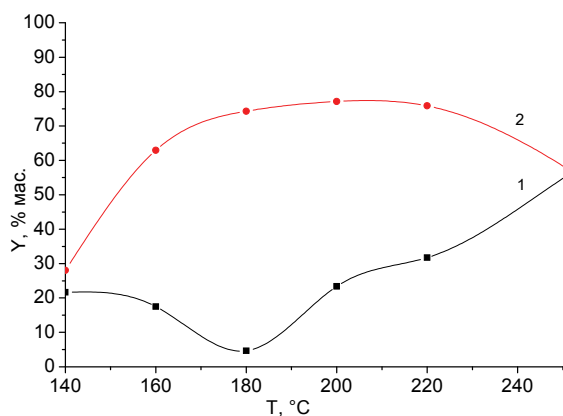


Fig.1 The yield of hexane isomers on catalysts with different amounts of impregnations; 1 - one impregnation Al_2O_3 , 2 - two impregnation

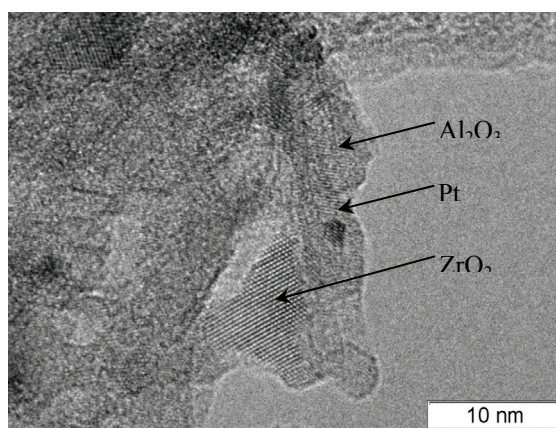


Fig.2 The TEM $\text{Pt/SZ/Al}_2\text{O}_3$ - two impregnation Al_2O_3

Catalytic Epoxidation of Methyl Oleate with Hydrogen Peroxide under Phase Transfer Condition

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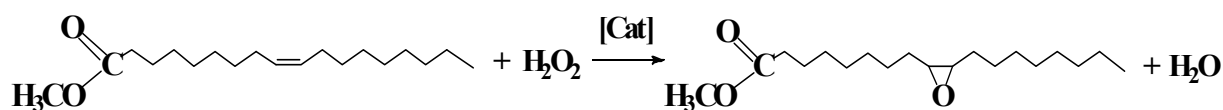
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One of the most promising methods of oxidation of organic substances with aqueous hydrogen peroxide nowadays is phase transfer catalysis method (PTC) using homogeneous bifunctional catalysts based on peroxopolyoxometalates and quaternary ammonium cations [1]. Using this method allows to carry out oxidizing reactions in biphasic organic-aqueous systems in one step. Such reactions proceed at mild conditions: at atmospheric pressure with temperature not exceeding 100°C, sometimes even without organic solvents. With that, high conversion and selective rates are attained. Therefore catalytic oxidation with hydrogen peroxide processes at such conditions are environment-friendly.

Such catalytic systems have been proved to be highly effective for epoxidation of unsaturated hydrocarbons such as for example unsaturated fatty acids or its ethers [2], [3], [4]. Unsaturated fatty acids appear in tall oils, which are part of industrial wood residue.

This paper examines kinetics of methyl oleate catalytic oxidation with 30% H₂O₂ aqueous solution resulting with epoxide (which is in demand for plastic and varnish-and-paint material manufacturing) as a target product.



Oleic acid is among principal components of tall oils which are co-products of sulfate/sulfite processes applied in wood processing for cellulose preparation.

Tetrakis(oxodiperoxotungsto) phosphate complexes with quaternary ammonium cations were used as a catalyst. Catalyst synthesis was performed in accordance with [5]. The structure of complexes obtained was testified by IR-spectrometry methods and element analysis.

OS-5

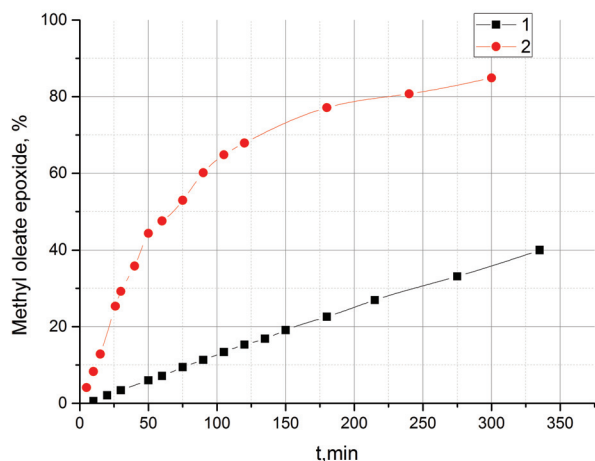


Fig.1 Oleic acid methyl ether epoxide content (ω , %) versus time for (1 –Cat1, 2- Cat2)

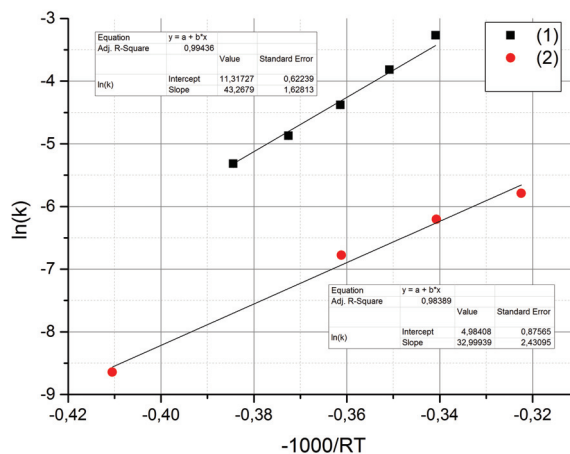


Fig.2 MO epoxidation rate constants versus time in Arrhenius coordinates (1 –Cat1, 2- Cat2)

The highest catalytic reactivity in methyl oleate epoxidation was shown by tetrakis (oxodiperoxotungsto) phosphate methyltri-n-octylammonium $[Me(n-Oct)_3N]_3\{PO_4[WO(O_2)_2]_4\}$ (Cat1) and hexadecylpyridinium - $[C_{16}H_{33}N(CH_2)_{15}CH_3]_3\{PO_4[WO(O_2)_2]_4\}$ (Cat 2). For this catalysts apparent reaction rate constants were $(1.22 \pm 0.04) \times 10^{-2} \text{ min}^{-1}$ and $(1.72 \pm 0.04) \times 10^{-3} \text{ min}^{-1}$ and observed activation energy values were $43 \pm 2 \text{ kJ} \cdot \text{mol}^{-1}$ and $33 \pm 2 \text{ kJ} \cdot \text{mol}^{-1}$ respectively.

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Triethanolamine Producing in Microchannel Reactor

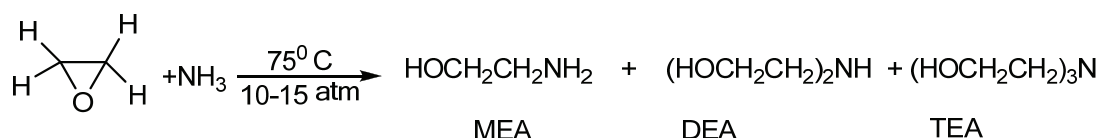
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Micro reactor technic is a promising approach to enhance the ecological safety of the processes of fine chemicals synthesis. Because of small reaction volume, the accurate adjustment of process parameters such as feed rate of reagents, temperature, pressure, and residence time in micro reactors can be performed without undesirable delays affecting the product quality. The efficient heat transfer provides the absence of the overheated zones and, therefore, the avoidance of thermally induced undesired side reactions. Scaling using micro reactors is a simple increase of reactor number that doesn't require the tryout of the process parameters for the extended reaction volume. All that features allow considering micro reactor technic as a safe, low waste, environmentally benign method for the producing of valuable chemicals.

Triethanolamine (TEA) is one of the industrial scale products which can be synthesized using micro reactors. TEA is used for entrainment of industrial gaseous waste emissions, as plasticizer, and as a reagent in pharmaceutical and cosmetic industry. TEA has to satisfy a number of stringent requirements. The most important ones are the color index and TEA content in the product. The existing process is based on the reaction of aqueous ammonia with ethylene oxide in static autoclave of periodic action. It resulted in formation of the mixture of ethanolamines with the different alkylation degree and the desired product is isolated from the products mixture by vacuum distillation [1, 2].



We have studied the process of TEA producing in a micro-channel reactor. Reaction of ethylene oxide ammonolysis was carried out in water acting as a reaction media and as a catalyst. It was found, that the optimal feed rate of reagents for TEA formation is 0.5 ml/min for ammonia solution and 1.0 ml/min for ethylene oxide. In that conditions at the 3 minute contact time in reactor TEA was obtained with yields more than 90%. The product has low color indexes (10 by Iodine scale). Besides, varying of the contact time in the developed process can be used for selective producing of mono- and diethanolamines, which have their own value as intermediates in the synthesis of bioactive compounds.

The work is supported by RAS Program of basic researches, project N 5.7.4 and State Contract № 9208.1007900.13.1099 from 19.08.2009

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Linear Alkylbenzenes Manufacturing Unit Work Optimization with Use of Computer Modeling System

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Optimization of linear alkylbenzenes manufacturing unit is an important for enhancing the yield and quality of synthetic detergents. In our case optimization consisted in determination of optimal value of water supply into paraffins dehydrogenation reactor and providing of the stable work of the «reactor-regenerator» system of benzene with olefines alkylation unit.

Over the last years there has been a great progress in the development of environmentally friendly processes of alkylation of aromatic compounds with olefins. The most demanded products of petrochemical synthesis are based on synthetic detergents produced from linear alkylbenzenes (LAB). Such detergents have good foamability and high biodegradability, this makes the task of the increasing the efficiency of LAB production very important. In addition, technology involves a number of auxiliary stages, the importance of which is comparable to the importance of the main stages, as they determine operating condition of the system. One of such stages is the regeneration of HF-catalyst of alkylation process in rectification column. Complex of LAB manufacturing includes following technological stages: paraffins dehydrogenation over the Pt-catalyst, diolefines selective hydrogenation and alkylation of benzene with olefins using the HF-catalyst.

The optimization of LAB manufacturing was carried out with the use of the mathematical model of these processes, which was developed based on physical and chemical laws of hydrocarbons conversion into account. The study carried out using described modeling system allowed to reveal following peculiarities.

It was determined that at initial operating period of dehydrogenation catalyst optimum amount of water must be 4 l/h at a process temperature of 467 °C, whereas the process temperature increases by 20 °C compared with the original, the amount of water fed to the reactor should be 9 l/hour. Predictive calculation of lifetime of dehydrogenation catalyst showed that the increasing of water amount would increase the lifetime by an average of 15-20%. When using an alkylation catalyst with activity of 0.88, achievement of critical temperature at the bottom of the column and, therefore, the operation mode failure occurred on 23.05.2012. If catalyst optimal activity had been 0.6 relative units, maintaining mode failure would have happened a month later – on 20.06.2012.

Thus, optimization of alkylbenzenes manufacturing unit consists in prolongation of the resource of dehydrogenation catalyst as well as the stable operating period of the HF-regeneration column.

Mathematical Modelling of Soot Deposition in Diesel Particulate Filters and Catalyzed Oxidation of Captured Soot

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The use of monolith soot filters is very promising to abatement of the amount of soot particles in diesel engine exhaust. Accumulated in pores of filter material, soot increases the pressure drop in a filter. In this case the burning of soot inside the filter is needed. To force soot burning at not high enough diesel exhaust gases temperature catalytic oxidation is necessary. The mathematical modelling of soot trapping in filter porous medium and catalyzed oxidation of captured soot via $\text{CeO}_2/\theta\text{-Al}_2\text{O}_3$, $\text{Pt-CeO}_2/\theta\text{-Al}_2\text{O}_3$ and $\text{Fe-Mn-K-O}/\gamma\text{-Al}_2\text{O}_3$ catalysts was done. Two major types of filters: wall-flow monolith with filtering exhaust gases through channel walls and monolithic block and three different filter porous media were considered: foam, fibers and grain structure (Fig. 1).

The mathematical model includes unsteady-state differential equations for polydisperse soot particles, O_2 and CO_2 concentrations in gas phase, soot content in solid phase, filter temperature and pressure drop. The heat balance accounts for heat transfer through convection and heat release by soot oxidation. Mass balances of gas phase compounds (soot, O_2 , CO_2) include mass transfer through convection, changes in O_2 and CO_2 concentrations due to soot oxidation, decrease in soot concentration by collecting of polydisperse soot particles, which consists of three main mechanisms: inertial impaction, interception and Brownian diffusion. Deposited soot equation takes these mechanisms into account as well.

The next parameters for wall-flow monolith: thickness of the channel walls 0,43 mm, exhaust gas velocity 0,7 m/s and for monolithic block: length 2,3 cm, gas velocity 0,7 m/s were used. Operating conditions were: exhaust temperature = 200 °C, O_2 concentration = 8 % vol., soot feed concentration 0,13 g/m³, particle size distributions was corresponded to gases generated by acetylene-burner with median particle diameter (μ_p) = 0,17 μm and standard deviation of particle size distribution (σ_p) = 1,74.

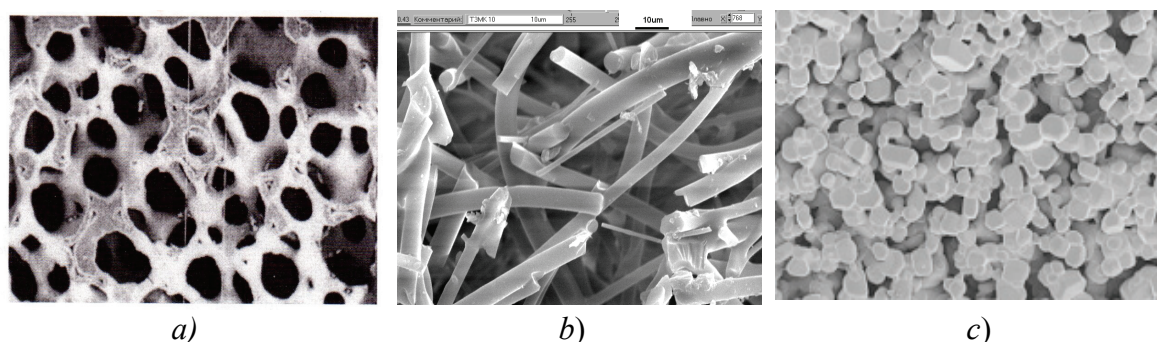


Fig. 1. Micrography of the filtering medium
 a) mullite; b) fiber quartz; c) carbide of silicon SiC [<http://www.ceraclean.com>]

Characteristics of filter porous material and simulation results are listed in Table 1. In accordance with numerical analysis of monolithic blocks, based on all examined porous materials, high efficiency of trapping of soot particles, $\theta \approx 100\%$. However, pressure drops, ΔP , both across the fiber quartz monolith and carbide of silicon one are larger than the allowed value. This is because fiber quartz has a small median fiber diameter and SiC has low porosity.

Characteristics of filter material and simulation results

Tabl.1

Parameter		ZTA	mullite	fiber quartz	SiC
porosity, %		80	80	86	37
Median pore diameter, mkm		3,1	4,5	10,0	10,3
Median diameter of fiber and grain or "equivalent" fiber for foam, mkm		6,3	6,3	4,4	10,2
θ at the end of the process, %	monolithic block	100	100	100	100
	wall-flow monolith	22	22	38	34
ΔP , Pa	monolithic block	1760	1270	$>\Delta P^*$	$>\Delta P^*$
	wall-flow monolith	0,9	0,7	2790	290

According to specifications, the allowable limit on pressure drop ΔP^* in an engine exhaust system is equal to 10000 Pa.

Besides, mathematical modelling of catalytic oxidation of trapped soot via $\text{CeO}_2/\theta\text{-Al}_2\text{O}_3$, $\text{Pt-CeO}_2/\theta\text{-Al}_2\text{O}_3$ and $\text{Fe-Mn-K-O}/\gamma\text{-Al}_2\text{O}_3$ catalysts was done. The used kinetic parameters are listed in Table 2 [1].

Kinetic parameters [1]

Tabl. 2

Catalyst	E_A , kJ/mole	k_0 , $(\text{g}_{\text{cat}} \cdot \text{s} \cdot \text{atm})^{-1}$	α	β
$\text{CeO}_2/\text{Al}_2\text{O}_3$	160,8	$0,2 \cdot 10^9$	0,5	0,9
$\text{Pt/CeO}_2/\text{Al}_2\text{O}_3$	111,4	$0,2 \cdot 10^6$	0,6	0,8
Fe-Mn-K-O	128,7	$0,1 \cdot 10^9$	0,5	1,0

[1] T.L. Pavlova, N.V. Vernikovskaya, A. Ermakova, V.V. Mokrinskii, V.N. Kashkin, A.S. Noskov, Kinetic modelling of catalyzed oxidation of soot, International Conference Nanostructured catalysts and catalytic processes for the innovative energetics and sustainable development, June 5–8, Novosibirsk, Russia, 2011, Abstracts: Print-CD volume, PP-21, (2011) p. 62.

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ABSTRACTS

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