Institut Français du Pétrole

ADIFP (Associations des Doctorants IFP)

July 4 - 9, 2011 Institut Français du Pétrole

Lyon France

The Second French-Russian Workshop on Catalysis, Petrochemistry and Renewable Energy for Young Scientists

Lyon - 2011

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IFP Energies nouvelles, Lyon

ADIFP (Associations des Doctorants IFP)

Novosibirsk State University

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Invitation

The Second French-Russian Workshop on Catalysis, Petrochemistry and Renewable Energy for Young Scientists will be organized in Lyon, France on July 4^{th} – 9^{th}, 2011 at IFP Energies nouvelles.

The Workshop will give emphasis on the actual topics of research in the areas of catalysis, oil processing and renewables. The Workshop intends to educate with the lectures, visits, and short training courses at research institutes of Lyon to give students and young scientists the chance to present their work to and communicate with authorities in the field of workshop topics and each other and will allow to develop the relationships between young researchers of France and Russia.

The first Russian-French Workshop on Catalysis, Petrochemistry and Biomass for the young scientists was successfully held in Omsk and Novosibirsk (Russia) between 18th and 24th of May 2010 and organized by Boreskov Institute of Catalysis (Novosibirsk, Russia).

The Workshop will consist of invited lecture and selected oral and poster presentations of young scientists. The sessions will be organized on the basis of the participation in the different topics concerning Oil, Catalysis, Renewable energy, Biofuel, Petrochemistry. During the Workshop visits to different researches institutes, such as IFP Energies nouvelles, (IFP-Lyon), Institute of Research on Catalysis and Environment (IRCELyon), Claude Bernard University Lyon 1, C2P2 (Chimie, Catalyse, Polymères et Procédés) and the Lyon Center for High Field NMR will be organized for participants.

To promote poster contributions, a continuous poster session will allow lively discussions andnetworking throughout the workshop. Awards will be attributed to the best young scientist contributions.
We are looking forward to meeting you in Lyon!

Invited speakers
Bernadette CHARLEUX, CNRS-University of Lyon, France

Claude MIRODATOS, CNRS-University of Lyon, France

IFPEN solutions for lowering the cost of postcombustion CO_2 capture
Pierre-Louis CARRETTE, IFP Energies nouvelles, France

Design of functional porous materials for CO_2 capture and catalytic valorization
David FARRUSSENG, CNRS-University of Lyon, France

The Time table of the French – Russian Workshop
04 -09 July, 2011

5 July
Opening of the Workshop
OP 1. Sofya A. Khromova
OP 2. Natalya V. Mezentseva
OP 3. Marina V. Bukhtiyarova
OP 4. Ksenia M. Kaprielova
OP 5. Pavel A. Kolinko
OP 6. Laure Braconnier
OP 7. Rim Brahem
OP 8. Caroline Besson
OP 9. Maria Braga
Poster session

6 July
OP 11. Victoriya O. Dundich
OP 12. Ivan N.Voropaev
OP 13. Irina V. Deliy
OP 14. Marina Yu. Smirnova
OP 15. Mariya M. Zyryanova
OP 16. Marie Savonnet
OP 17. Fabien Corvaisier
OP 18. Charles-Henri Nicolas
OP 19. Nicolas Thegarid
OP 20. Igor Y. Skobelev

Oral

#1

CATALYTIC PROCESSES FOR BIOFUELS PRODUCTION

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Today renewable feedstocks attracts much attention due to increasing of fossil fuels cost and its non-renewable nature, but the technologies level of biomass processing into engine fuels is still lower than for 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 and their competition with food sector plays negative role for bioenergetics progress. So, it's important not only to improve existing technologies, but also develop new biomass processing technologies with the expansion 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 following investigations in the field of catalytic renewable feedstock processing are carried out:

- high-cetane fuels production from biodiesel and plant oils directly, this technology is based on catalytic transetherification (in the presence of heterogeneous basic catalysts under 200-220ºC and 2.0 MPa) and mild hydrocracking (300-340ºC and 2.0 MPa H_2) and allows to obtain two types of fuels: biodiesel and green diesel,
- upgrading of bio-oil – product of plant biomass flash pyrolysis. High oxygen content and chemical complexity of pyrolysis oil make it unsuitable for direct use as a fuel. The quality of bio-oil can be improved by the catalytic hydrotreatment or hydrodeoxygenation (HDO). Typical catalysts for this process are sulfided Co - Mo and Ni – Mo, the main problems of these catalysts are rapid deactivation caused by sulfur loss and coke formation. Thus, the main objective within this direction is development of new non-sulfided catalysts. Synthesized Ni-based catalysts allow decreasing oxygen content in pyrolysis oil from 40 to 12 % wt.
- plant fatty acids conversion into fatty alcohols - valuable products for detergents, cosmetic and pharmaceutics. The reaction with the oleic acid in the presence of $Rh\text{-}B\text{-}Sn/Al_2O_3$ at the 250-400^{0}C and 80 MPa of H_2 gives the yield of oleyl alcohol up to 40%.
-production of carbonaceous materials.

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

#2

CATALYTIC TRANSFORMATION OF BIOFUELS TO SYNTHESIS GAS AND HYDROGEN

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Transformation of biofuels into syngas or hydrogen is one of the most important tasks of catalysis in the energy-related fields. However, due to a high reactivity of oxygenates a heavy coking is observed leading to the catalyst deactivation. Catalysts comprised of precious metals and/or Ni supported on fluorite-like or perovskite –like complex oxides with high lattice oxygen mobility are known to be very efficient and stable to coking in autothermal/steam/dry reforming of a variety of fuels. Monolithic substrates with a good thermal conductivity are promising for providing an efficient heat transfer within the reactor to prevent emergence of hot spots/cool zones deteriorating performance. This work presents results of research aimed at design of such catalysts and characterization of their performance parameters in transformation of a variety of fuels (mainly natural gas and liquid fossil fuels) at lab-scale and pilot-scale levels.

Nanocomposite active components were comprised of complex fluorite-like oxides $Ln_x(Ce_{0.5}Zr_{0.5})_{1-x}O_{2-y}$, perovskite –like oxides $La_{0.8}Pr_{0.2}Mn_{0.2}Cr_{0.8}O_3$ and/or NiO+YSZ prepared via modified Pechini route. Precious metals (Pt, Pd, Ru) were supported by the incipient wetness impregnation. Samples were characterized by BET, XRD, TEM with EDX, C_2H_5OH (1% in He) TPR and their subsequent TPOx by H_2O (1% in He). Several types of heat-conducting substrates including compressed Ni-Al foam, fechraloy foil or gauze protected by corundum layer, Cr-Al-O microchannel cermets were used for preparation of monolithic catalysts. These catalysts were tested in the reactions of autothermal/steam reforming of natural gas, reformulated gasoline, acetone, ethanol, anisole and sunflower oil using flow kinetic installations and specially designed reactors including a pilot tubular stainless steel reactor equipped with the electric current heated fuel/water evaporation unit and heating coils to change the catalyst temperature up to 1000^oC.

The authors gratefully acknowledge support from OCMOL FP7 EC, Project 57 of Presidium RAS and 02.740.11.0852 of the Federal Program "Scientific and Educational Cadres of Russia.

Oral

#3

TRANSESTERIFICATION OF RAPESEED OIL BY METHANOL CATALYZED BY BASIC SOLIDS M-Al-O (M = Sr, Ba, La)

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Nowadays, biodiesel obtained by transesterification of vegetable oil by alcohol over heterogeneous basic catalysts has gained significant attention as an environmentally benign substitute for petroleum-based fuels [1]. Such catalysts can be hexaaluminates $MAl_{12}O_{19}$ (M = Sr, Ba, La) which are characterized by high thermostability and acid-base properties.

The aim of the work was to compare structural, basic and catalytic properties of binary systems on basis of M-Al-O (*M = Sr, Ba, La*) for the transesterification reaction of rapeseed oil.

Experimental

Samples were prepared by precipitation of soluble nitrates of *M* and Al at pH = 7.5 – 8 and 70°C with NH_4HCO_3. The dried samples were calcined at 700 and 1200°C for 4 h. Structure, texture and acid-base properties of the samples were characterized by X-ray diffraction (XRD), nitrogen adsorption and Fourier transform infrared (FTIR) spectroscopy. Transetherification of rapeseed oil by methanol was carried out in the flow fixed bed reactor at 20 atm, 200°C.

Results and discussion

The study of hexaaluminate activity has shown that conversion of rapeseed oil increases with calcination temperature (T_{calc}) of the samples that can be related to some factors. According to XRD, the T_{calc} increase from 700 to 1200°C results in formation hexaaluminate phase which is accompanied by the changes of surface properties. According to FTIR spectroscopy, T_{calc} increase from 700 to 1200°C promotes disappearance of carbonate groups which are blocked the active basic sites. Therefore, all surface acid and base sites reveals the activity. Accessibility of the sites increases owing to increasing amount of large pores. The increased activity of Ba-hexaaluminate is related to presence of the basic sites with the higher strength and the lowest concentration of Lewis acid sites that is confirmed by FTIR spectroscopy.

References:

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#4

IMPROVING Pt CATALYSTS FOR GREEN OXIDATION OF ALCOHOL

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The catalytic oxidation of alcohol with oxygen as the oxidant and water as solvent – ideal conditions for economy, environment and safety – is a challenging task in fine organic synthesis, energy technologies, environmental science, and other important fields. The catalyst productivities are still below the level of cost-efficiency. Especially, oxidation of primary and secondary aliphatic alcohols at ambient temperature proceeds with turnover frequencies 1-100 h^{-1} and stops at low/moderate conversions, due to severe deactivation of the catalysts. Here we show that excellent catalytic performance is possible even with the low-reactive substrates, while retaining the reaction conditions mild and green. Moreover, it is achievable even with conventional and non-promoted Pt/C catalysts, provided that conditions of their synthesis, pretreatments and testing were properly adjusted.

The examples given in the Figures refer to catalysts which have been prepared from the traditional metal precursor (H_2PtCl_6) and on an ordinary activated carbon as the support (Norit). In a sharp contrast to what might be expected from previous studies with iso-propanol (IP), 97-99% of this non-activated alcohol can be converted in a few minutes (achievable for a longer time 99.9%), simultaneously with catalyst reuse and turnover frequencies TOF_t (per all Pt atoms) as high as 2500-5000 h^{-1} for a whole run (TOF_s per surface Pt atoms up to 80000 h^{-1} at the beginning of the runs).

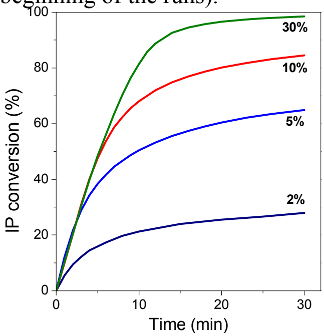

Fig. 1. Catalytic performance of Pt/C samples prepared through hydrolytic deposition and differed in Pt loading (wt% near the curves). Conditions: H_2O 9.5 ml, IP 6.5 mmol, O_2 1 bar, 30 °C. Catalyst mass 5-75mg but the mass of Pt constant (7.5 μmol)

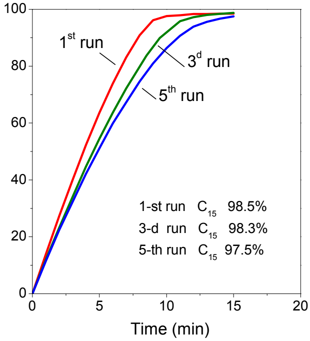

Fig. 2. Performance of a 5%Pt/C catalyst in five successive runs. Preparation via reductive deposition. The same conditions of testing as in Fig. 1; catalyst mass 20 mg (Pt 5 μmol)

Oral

#5

TITANIUM DIOXIDE MODIFIED WITH NOBLE METALS IN ETHANOL VAPOR PHOTOOXYDATION UNDER VISIBLE LIGHT

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Photocatalysis is one of the promising methods for destruction of toxic pollutants. TiO_2 is the most active metal oxide semiconductor among heterogeneous photocatalysts. It is playing an important role in many industrial and technological processes, environmental and biomedical applications. Pure TiO_2 photocatalysts is active only under the UV irradiation with photons of energy equal or higher than its band gap (3.2 eV). Unfortunately ultraviolet or near-ultraviolet radiation occupy only about 4% of the solar light spectrum [1]. In order to efficiently utilize solar light in the visible region ($\lambda > 400$ nm) which covers large range of the solar spectrum, the development of visible-light-driven (VLD) photocatalysts was began to study over last decades.

A good method is doping of titanium dioxide with nitrogen (N), carbon (C) and sulfur (S) atoms [2] thus making an additional energy levels in the semiconductor band gap but this method leads to an increase of recombination rate of photoinduced electron-hole pairs. As a result the overall quantum efficiency reduces. In recent years, increasing attention is paid to the development of new photocatalysts for visible light based on the TiO_2 doped with transitional metals or their ions [3, 4]. Metals contribute to the increase of charges carriers separation efficiency and to the appearance of an additional electronic levels in the energy structure of semiconductor. Also metal particles could act as a chemisorption centers and increase adsorption efficiency of doped TiO_2.

Different TiO_2 based photocatalysts were synthesized in the present work by the TiO_2 impregnation with transition metal oxides (Ru, Pt and Pd) and TiO_2 doping with noble metals like Ag, Au, Pt, Pd by the chemical and photochemical deposition methods.

Many samples demonstrated the adsorption capacity and activity in visible light region comparable with commercial TiO_2 (Kronos vlp 7000). The specific activity of Au/TiO_2 samples in the reaction of ethanol vapour PCO was even higher than for pure TiO_2. Acetaldehyde was demonstrated to be the only gaseous intermediate of ethanol photocatalytic oxidation.

It was shown that complete ethanol vapour mineralization could be achieved in a static reactor with the use of Au/TiO_2 photocatalyst for 900 minutes with the formation of carbon dioxide and water as final products.

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#6

ORIENTATION OF THE CRYSTALLINE PHASE DURING COBALT CATALYSTS ACTIVATION FOLLOWED BY *OPERANDO* XRD AND DRIFTS

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An increasing interest in the Fischer-Tropsch FT process has been observed for the last 10 years. The constant rise in fossil fuels' price and the need to diversify the fuel resources are at the heart of this interest. Fischer-Tropsch synthesis allows the transformation of syngas into high molecular weight hydrocarbons with the use of heterogeneous cobalt supported catalysts. The FT waxes can afterwards be up-graded into high purity kerosene and diesel pool.

Catalytic properties of cobalt supported catalyst depend mainly on the morphologic and structural properties of metallic cobalt nanoparticles [1]. Most of the time, they consist of cubic and hexagonal crystalline phases with stacking faults [2]. Due to these characteristic structures the catalytic properties of the catalysts cannot be easily linked to their structural properties.

In this present work the activation parameters were modified to orient the metallic cobalt crystalline structure towards either a pure cubic phase or a pure hexagonal phase.

An innovative coupling with XRD and DRIFTS techniques has been specifically developed for this study. The use of a reaction cell supporting high pressure and high temperature has allowed *operando* catalyst characterization in representative activation conditions. By choosing the reduction gas, metallic cobalt structure has been oriented towards a cubic crystallographic phase. During the rise in temperature, reduction took place under an inert atmosphere. When step temperature was raised, the gas was switched into pure hydrogen. The XRD diagram recorded after this activation process showed enrichment in cubic phase and a diminution in the hexagonal diffraction peaks (figure 1).

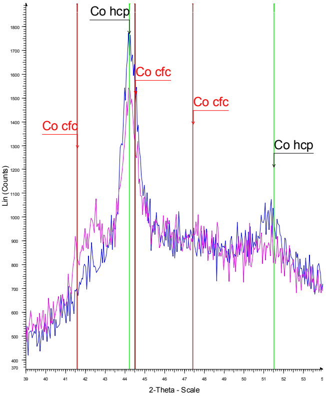

Figure 1 : XRD diagrams obtained after reduction of a Co/SiO$_2$ catalyst at 550° under pur H$_2$ (pink) and under inert gas then under pur H$_2$ (blue)

The pure hexagonal phase was obtained after a reduction stage under H$_2$ at 550°C and a carbide cycle composed of carbide formation at 230°C under pure CO and carbide decomposition at 230°C under pure H$_2$.

Even if the cobalt crystallographic phase has been well oriented, some crystallographic faults still exist. These faults are being quantified by the use of XRD diagram simulation software (SIMVAXS) [3].

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Oral

#7

EXPERIMENTAL AND NUMERICAL STUDY OF COLUMN TRAYS: DEVELOPMENT OF SCALING LAWS

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For gas treating processes, taking into account the lower gas specifications (environmental constraints, increase of the LNG market), an optimization of the process is required. Trays, and more specifically valve trays, are widely used. Both fluids, the gas flowing in the upward direction and the liquid flowing in the downward direction, are contacting each other and operate far from hydrodynamic limitations.

An increase in mass transfer on the tray will consequently leads to a real increase of the efficiency.Moreover, literature proposes mass transfer correlations with very different forms, in particular in the way of taking the liquid phase into account. A better understanding of the hydrodynamic is thus required.

The thesis work will be done in three steps :

- First, global and local experimental data must be acquired on trays on units available at IFP. Original measurements methods will have to be used for mass transfer coefficients but also local hydrodynamics characteristics (void fraction, speed, drop/bubble sizes ...). On one hand, these measurements will allow to determine the physical characteristics controlling hydrodynamics and mass transfer and to develop associated correlations to allow extrapolation of laboratory experiments to industrial cases. On the other hand they will feed the numerical simulation.
- Second, original closure laws must be proposed to take into account the gas/liquid interactions depending on the different operating parts of the tray.
- Last, the developed models will be implemented in the Fluent CFD software as user-defined functions. Once done, this work will be validated against pressure drops curves, flooding, void fraction profile, tracing and all over local measurements. If time still available, taking the mass transfer into account will be a last validation. A numerical parametric study will enlarge the validity of the scales law experimentally obtained.

This work will lead first to a real competences development on trays of absorption column, secondly to model and scaling laws for extrapolation to industrial operating conditions (fluids, sizes, pressure ...) with confident. This thesis will also allow to test future original designs of trays easily and rapidly with the numerical model developed.

#8

DIRECT COAL LIQUEFACTION

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Modern processes of DCL are two-stages processes. Coal is mixed with a solvent. In a first reactor, the blend is heated up to 400-450°C under high hydrogen pressure (150-200 bars). Coal liquefies. Then in a second reactor, coal liquids are converted to lighter and purer products, by severe hydrotreatment. Both steps are catalytic. Coal liquids are then distillated, to recover naphta and gasoil fractions. Heavier fractions are recycled in order to be the solvent of the reaction. This work aims at studying the first stage: impact of operating conditions and impact of the solvent. The characterisation of products is also a challenge.

To study coal liquefaction, a 500mL stirred autoclave reactor is used. The coal selected is an Illinois n°6, the solvent is 1,2,3,4,tetrahydronaphtalene (tetralin). Catalyst is a sulphided Ni/Mo on $Al2O3$. Classical operating conditions are 160 bars, 400°C and 3 hours of test. The product mixture is centrifuged to collect light liquids. Heavy liquids are collected by Soxhlet extraction. All products are analysed. In classical conditions, a test leads to a conversion of 82%. In more severe conditions (i.d. 450°C and 8 hours) it can reach 97%. Liquid products are separated by distillation.

Pi-220°C is the solvent fraction. 220°C+ fraction is divided by liquid-liquid extractions in order to quantify the amount of oils, asphaltenes and preasphaltenes. These fractions are mostly aromatic and naphteno-aromatic. The influence of temperature, pressure, solvent will be showed.

There are many parameters impacting yields in valuable liquids. Characterisation of products is also challenging and understanding the whole chemistry of direct coal liquefaction still need a lot of work. Nevertheless, industrial units are starting these years (Shenshua, China), showing that this route to alternative fuels becomes economically promising.

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#9

STUDY OF HYDRODYNAMICS AND EXTERNAL TRANSPORT PHENOMENA IN A CATALYTIC BASKET LABORATORY REACTOR

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The scale-up of industrial triphasic catalytic fixed bed reactors and the performance evaluation of commercial shaped catalysts requires catalytic tests at laboratory scale reactors usually performed under industrial operating conditions. Among the laboratory reactors which allow to operate with commercial on shaped catalysts, batch stirred tank reactors are often used. In these reactors, the solid catalyst is immobilized in a stationary annular basket and the fluids circulations through the basket is ensured by impeller stirring. In this kind of reactors, temperature and concentrations gradients in the liquid phase might occur due to unsuited configuration and/or operating conditions. Moreover, the hydrodynamics (e.g. liquid phase velocity between the impeller and the catalytic basket) and external mass transfer G/L (k_La_L) end L/S (k_S) of these reactors are insufficiently characterized to predict them.

The aim of this study is the determination of the applicability field of different stirred tank reactors with catalytic basket. For this propose, a complete parametric study (CFD simulations + laboratorial experiments) will be realized to evaluate the influence of the reactor configuration (e.g. type of impeller, type of catalytic basket, gas injection location, etc) on hydrodynamics and external mass transfer.

This study will enable us to better understand the external mass transfer phenomena on actual batch stirred tank reactors with catalytic basket and to define design rules that will allow us to optimize and intensify this kind of tool, choosing the optimal design according to the considered application.

#10

CHEMICAL LOOPING COMBUSTION, A PROCESS WITH INHERENT CARBON DIOXIDE SEPARATION

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Chemical looping combustion (CLC) is a promising novel combustion technology involving inherent separation of CO_2 with minimum energy penalty. An oxygen carrier is employed to continuously transfer oxygen from air reactor to fuel reactor where oxygen is delivered to the fuel. Consequently direct contact between air and fuel is prevented. The resulting flue gas is CO_2 rich and not diluted with N_2. The reduced oxygen carrier is then transported back to the air reactor for re-oxidation purpose, hence forming a chemical loop.

Various CLC configurations have been already developed and tested in laboratory pilot plant scales. However more investigations are required to improve knowledge and to achieve optimized process operation. Among the different points to address, selection of the oxygen carrier particle, control of solid circulation rate and gas tightness are of highest importance. Aspects of the oxygen carrier and important selection criteria are discussed. Moreover different possible feeds in CLC process and associated reactions are briefly presented. Finally, some of the existing CLC pilot plants in the world are studied. Different aspects of each design is stated. A new CLC concept is proposed and discussed for pilot plant, capable of controlling solid flow rate while minimizing the gas leakage.

Oral

#11

CATALYTIC HYDRODEOXYGENATOIN OF PLANT FATTY ACIDS DERIVATIVES

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Nowadays it becomes more perspective to produce engine fuels from the renewable sources. The first direction of the present work is devoted to the biodiesel hydrodeoxygenation process study. The biodiesel is a mixture of methyl esters of fatty acids (FAMEs). In spite of a number of its ecological advantages, biodiesel cannot be used in diesel engines without modernization of the engine. The main reason for the quite low operating characteristics of biodiesel is high oxygen content due to the presence of ester groups (11-12 %wt.) in its components. Therefore the FAMEs can be used as a fuel for diesel engines only in a mixture with the hydrocarbon fuels. It should be noted that in contrast to the oil refining it is desirable to use non-sulfided catalysts in this process because of the low sulfur content in the biodiesel. Therefore the development of the new catalysts for biodiesel hydrodeoxygenation (HDO) is the aim of the present work. The reaction was carried out with the commercial biodiesel produced from the colza oil. The results of biodiesel hydrodeoxygenation showed that the most active catalysts are Rh/CeO_2-ZrO_2 and Ni-Cu/CeO_2-ZrO_2. The biodiesel methanization at the hydrodeoxygenation process is the feature of the nickel-based catalysts. Introduction of copper into the nickel catalysts increases the temperature of the methanization process start from 300-320^{0}C to 390-410^{0}C. The main products obtained at the 270-400^{0}C and 0,5-1,5 MPa of H_2 were linear hydrocarbons C_{14}-C_{17}.

The second direction of this work is research and optimization of plant fatty acids hydrodeoxygenation process in order to obtain fatty alcohols. Fatty alcohols are valuable products used in detergents industry, cosmetic, and pharmaceutical applications. The reaction was carried out with the oleic acid in the presence of Rh-B-Sn/Al_2O_3. The results of oleic acid hydrodeoxygenation showed that the main products obtained at the 250-400^{0}C and 80 MPa of H_2 were oleyl alcohol (selectivity up to 40%), alkanes (selectivity up to 45%) and undesirable product – wax. Therefore the selection of the optimal condition for minimal wax yield is also the important aim of the present work.

The variation of the process conditions and nature of the catalyst modifier enabled to produce different hydrocarbon products. The obtained experimental data on the examined catalysts stability and selectivity makes it possible to make the conclusions about a possibility of the given process industrial realization.

#12

CATALYTIC BEHAVIOR OF CARBON SUPPORTED PALLADIUM IN THE HYDROGENATION OF SUNFLOWER OIL

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Partial hydrogenation of vegetable oils is important in the production of margarines, frying oils, shortenings, soap stock, industrial oils. The reaction mechanism of the process is complex because of the occurrence of many side reactions such as cis-trans geometrical isomerization and positional double bound isomerization. The main purpose of the partial hydrogenation of fatty oils is to obtain monounsaturated fatty acids (MUFA) from polyunsaturated ones. It is also important to produce fats with required amount of *trans*-fatty acids (TFA). Central characteristics of the catalysts of the process are total activity and selectivities towards TFA and MUFA. Industrial hydrogenation of fats and oils is based on Ni catalysts. Pd catalysts allow carrying out the hydrogenation of vegetable oils at milder condition (low temperature and hydrogen pressure) in comparison with Ni catalysts. Moreover, a Ni catalyst gives significant amounts of TFA and saturated fatty acids. Soluble nickel by leaching found in hydrogenated oils can react with triglycerides to form fat-soluble salts, which may be harmful [1].

The goal of the present work is to investigate the dependences of the solid fat content (SFC) and selectivities towards TFA and MUFA on the technological parameters of the hydrogenation of sunflower oil (SF): concentration of supported Pd-catalysts (1/10000-1/2500 g_{cat}/g_{SF}), agitation rate (700-1500 rpm), hydrogen pressure (2-5 bar) and temperature (120-180^{o}C).

Hydrogenation of sunflower oil over novel structured 1 % (wt.) Pd/C catalyst with the average metal particle size of ~2.4 nm, BET-specific surface area 360 m^2/g and average pore diameter 5.9 nm, was investigated.

It was found that the selectivities attain their maximum values at the following conditions: high temperature and concentration of the catalyst, low H_2 pressure and slow agitation, those imply reduced concentration of hydrogen in the oil. SFC is strongly influenced by the final product composition. Approaches for controlling the composition and melting behavior of the final product were defined.

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#14

HYDRODEOXYGENATION OF METHYL PALMITATE AND METHYL HEPTANOATE OVER SULFIDED $CoMo/\gamma$-AL_2O_3 AND $NiMo/\gamma$-Al_2O_3 CATALYSTS

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The blending of biofuels in the diesel pool has become more and more important in the past years due to several reasons: depletion of crude oil resources, environmental protection, possibility of rural supportive policies, utilization of the uncultivated lands, smaller CO_2-emission in the total life cycle, etc. Promising strategies for upgrading crude bio-oils could be the direct hydrodeoxygenation (HDO) to produce hydrocarbons or the co-hydrotreatment with petroleum fractions, such as gas oil, to achieve the technical and environmental fuel standards. The bio-oil co-hydrotreating process has been approached by applying typical hydrodesulfurization catalysts, such as sulfidied $CoMo/\gamma$-Al_2O_3 and $NiMo/\gamma$-Al_2O_3 at temperature range 300-600^oC and hydrogen pressure within 28-200 bars.

The object of the present work is a comparative study of hydrodeoxygenation methyl palmitate and methyl heptanoate as the representative model components over commercial sulfided $CoMo/\gamma$-Al_2O_3 and $NiMo/\gamma$-Al_2O_3 catalysts.

The catalytic HDO of methyl palmitate and methyl heptanoate were performed in a batch reactor at temperature 300-350^oC and hydrogen pressure 35 bars over $CoMo/\gamma$-Al_2O_3 and $NiMo/\gamma$-Al_2O_3, using *n*-tetradecane, *m*-xylene or hydrotreated diesel fuel as a solvent.

In HDO experiments the performances of sulfided $CoMo/\gamma$-Al_2O_3 and $NiMo/\gamma$-Al_2O_3 catalysts were compared in terms of conversion of methyl palmitate and methyl heptanoate, oxygen removal, products yield, concentration of normal alkanes in the liquid products. The effect of the different reaction conditions (temperature, concentration of reagents, solvent nature, etc.) on the products yield and distribution have been studied. The tentative reaction scheme of methyl palmitate transformation was considered in comparison with obtained for methyl heptanoate hydrodeoxygenation.

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#15

SULFATED ALUMINA AS AN EFFECTIVE CATALYST FOR THE ISOBUTANE/BUTENE ALKYLATION

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Sulfated oxides are considered as potential catalysts for the isobutane/butene alkylation and n-alkane isomerization. The majority of authors believe that sulfated zirconia (SZ) is the most active system in both reactions. At the same time sulfated alumina (SA) is reported as a catalyst with rather low activity. However, the comparison of SA and SZ with close surface sulfate density demonstrates that SA has much less isomerization activity than SZ but this system is more promising in the isobutane/butene alkylation [1]. It exhibits the same stability as SZ in this reaction but higher C_8 products selectivity.

Fast deactivation of solid acid catalysts in isobutane/butene alkylation requires continuous regeneration or decreasing of highly unsaturated species formation. For this goal, the noble metal modification and carrying out the reaction in the presence of hydrogen were applied for the zeolite REY [2]. This approach adapted to the alkylation over SA system allows increasing significantly SA stability without any negative influence to its C_8 selectivity (Fig. 1). However, this leads to the alkylate yield decreasing up to 1.6-1.7. In spite of this fact, $Pd/SO_4/Al_2O_3$ can be considered as a perspective system for the alkylation process with periodic catalyst regeneration.

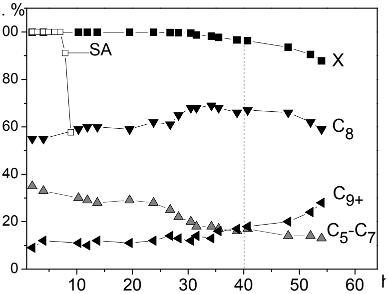

Fig. 1. Product distribution and butene conversion (X) over $0.9\%Pd/15.9\%SO_4/Al_2O_3$. Conditions: fixed bed reactor, WHSV($C_{4=}$)=0.02 h^{-1}, i/o=46/1, C(H_2)=1 mol.%

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Oral

#16

CATALYTIC CONVERSION OF CARBON OXIDES AND LIGHT HYDROCARBONS TO METHANE-HYDROGEN MIXTURES

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Methane-hydrogen mixtures production and optimization is considered as a relevant point of recerch for present moment. Its application includes feeding low temperature proton exchange membrane fuel cell (PEMFC) which requires CO concentration in gas mixture as low as 10 ppm due to poisonous effect of carbon monoxide. Hydrocarbons conversion as a main source of hydrogen produced yields hydrogen mixtures which contain CO at concentrations ~ 0,5 - 2 vol. % CO along with CH_4 и CO_2 (inert for fuel cells). Catalytic selective CO methanation is one of preferable ways for gas system optimization.

Assotiated gas conversion is another point of research especially relevant it terms of its emission reduction to the atmosphere. Process of assotiated gas convertion into methane-hydrogen mixtures with constant composition is a promissing way of utilization [1, 2]. Produced gas with high CH_4 content could be used as a fuel for electricity generation or transferred through gas pipe lines to the storage place for further processing or local habitants needs.

Series of Ni catalysts impregnated on different supports was prepared and tested in methanation reation. Experiments were held in fixed bed quartz reactor at atmospheric pressure. Gas concentrations before and after the reactor were measured with gas chromatograph. The most active system was chosen based on its activity and selectivity. The level bellow 10 ppm was achived in a wide temperature interval with high selectivity for gas mixture containing 1.5 vol. % CO.

Experiments with assotiated gas converion were carried out on a model gas mixture: 11.11 vol.% C_3H_8, 22.22 vol.% CH_4, 66.67 vol.% H_2O. Again Ni loded systems demonstrated good activity. Full propane conversion was observed at 280 ^oC and GHSV – 3100 h^{-1}. Outlet gas mixture contained 4.2 vol.% H_2, 85 vol.% CH_4, 10.6 vol.% CO_2, 0.2 vol.% C_3H_8.

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Acknowledgements

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#17

COMBINATORIAL SYNTHESIS OF MULTIFONCTIONAL MOF VIA A GENERIC POST-FUNCTIONALIZATION ROUTE.APPLICATION TO ACID/BASE CATALYSIS

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We have recently reported an original PSM method starting from amino derived MOFs. The first step consists in converting the amino group into azide (N3). Without isolation nor purification, the desired functionalized material is obtained by grafting a the corresponding alkyne using “Clik Chemistry”.

In this contribution, we show that our method can be applied to all kind of MOFs with respect to pore size range (micro to meso), chemical stability (low to high) and different degree of -structural flexibility and to all kind of grafted chemical functions (acid, coordinative, base, aromatic, aliphatic, hydrophilic).

- A diverse library of 48 original MOFs was synthesized and characterized.
- We show that we can control the grafting rate from 10 to 100%.
- For the first time, we report the effect of the grafting rate on the porous volume of the host MOF. This method was also used to engineer catalytic MOFs for the transesterification of ethyldecanoate with methanol. Results show the linear increase of conversion with the increase of the degree of modification. The best performances are obtained for a multi-functionalized MOF which combined an optimum basicity/hydrophoby balance.
- Finally, new solutions to enginneer catalytic site isolation will be presented.

Oral

#18

RATIONNAL DESIGN OF NEW METALLIC CATALYST FOR SELECTIVE HYDROGENATION

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Supported metal catalysts are used in many industrial processes (refining, petrochemicals, chemicals,…) and in most of post-treatment processes for environmental concerns (post-combustion, car converters,…). In the frame of refining, supported palladium catalysts are used for purification of light cuts through selective hydrogenation of polyunsaturated compounds. However, palladium is a rare and expensive metal. A possible way of innovation in this area is the discovery of news “drop-in” Pd free multimetallic formulations. At equal performances, the lower raw material cost of nobel metal freee catalysts will give competitive advantage on current catalysts. Besides, the development of these new systems open the perspective to achieve enhanced activity and selectivity compared with existing catalysts.

#19

NOVEL MEMBRANE-BASED PROCESSES FOR CO_2 CAPTURE IN VEHICLES

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One of the main strategies for mitigating climate change deals with the capture, transport and long-term storage of greenhouse gases (GHGs), noticeably CO_2. The available techniques for post-combustion CO_2 capture are highly energy-consuming (>4 GJ/tCO_2 recovered) and require much space (e.g., amines bath), therefore not being suitable for an on-board application. To reduce the energy demands and size of the separating units for a so-called application, membrane-based processes appear to be good candidates.

In this communication, we present the synthesis of nanocomposite MFI-alumina hollow fibres with promising selectivity towards CO_2 separation and high permeation performance. Hollow fibre geometries are outstanding for their higher surface/volume ratios compared to conventional tubular membranes. The zeolite material is here embedded into the fibres pores instead of forming a layer [1]. This confers to the final structure not only higher mechanical stability, but also an improved separation performance at higher temperatures.

The concept proposed here is an on-board CO_2 capture unit consisting in a cascade of 2 separation followed by a storage unit. According to our calculation, an abatement of 75% of the emitted CO_2 is feasible with a CO_2/N_2 separation factor of 20 and a permeance of 1 $\mu mol.m^{-2}.s^{-1}.Pa^{-1}$ [2].

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Oral

#20

TOMORROW'S BIOFUEL: BIO-GASOLINE PRODUCTION IN FCC UNIT

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Due to the depletion of carbon fossil resources and increased efforts to mitigate CO_2 emissions, new generations of fuels have recently been proposed, involving a partial replacement of fossil resources by renewable ones. Lignocellulosic biomass is a promising feedstock since it is abundant and cheap and can be transformed into fuels and chemical products. A major challenge is the required mass production given the huge capacities involved in transportation, which means that rapid change can only be achieved by using existing infrastructures. Therefore, a realistic scenario for bio-fuels mass production in the short term is "co-processing" of biomass-derived resources together with crude oil in standard refineries. Fluid Catalytic Cracking (FCC) converts high molecular weight hydrocarbons to more valuable products mainly gasoline. Pyrolysis-oil obtained from lignocellulosic is a potential candidate for co-processing, as the technology for producing them has been validated at pilot scale [1]. However, their lower heating value, immiscibility with hydrocarbon fuels, chemical instability, high viscosity and corrosiveness, due to their high oxygen content make the co-processing a challenge. Therefore to make them compatible with crude oil feed stocks, various upgrading processes have been investigated among which hydrodeoxygenation (HDO) able to reduce efficiently the oxygen content of bio-oils. This process uses considerable amounts of hydrogen and it is operated at elevated pressures. Therefore new pyrolysis routes are being investigated to obtain stable liquids with reduced oxygen content. In this study bio-oils obtained from catalytic liquefaction are studied under FCC co-processing conditions. Detailed product fractions have been obtained by GCxGC analysis for various carbon to oil ratios. The results are further compared to co-processing of HDO pyrolysis oil [2].

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#21

OXYDATION OF CYCLOHEXENE IN THE PRESENCE OF COORDINATION POLYMER Fe-MIL-101

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Coordination polymers are attractive materials to application in the heterogeneous catalysis[1]. In 2005 Férey and co-workers reported the synthesis[2] of mesoporous chromium terephthalate MIL-101. It contains large cavities (29 and 32 Å, respectively, Figure 2) and is stable to heating and different solvents.

Cr-MIL-101 was previously shown as a catalyst for allylic oxidation of unsaturated substrates with TBHP[3], effective support for $[PW_4O_{24}]^{3-}$ and $[PW_{12}O_{40}]^{3-}$ polyoxotungstates[4] and iron phthalocyanines[5]. In this context catalytic properties of Fe-MIL-101 are of interest.

Fe-MIL-101 material was prepared and characterized using XRD technique, IR spectroscopy and N_2-adsorption measurements.

In this work catalytic activity of Fe-MIL-101 has been investigated. It was found that Fe-MIL-101 is active in aerobic oxidation of cyclohexene in mild conditions. The main products of this reaction are cyclohexenone (30-40%), cyclohexene hydroperoxide (30-40%) and cyclohexenol (20-40%) (Figure 3). Hot catalyst filtration test shows that this catalyst was truly heterogeneous.

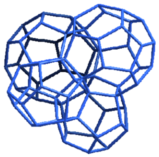

Figure 2. Schemaic structure of MIL-101 material

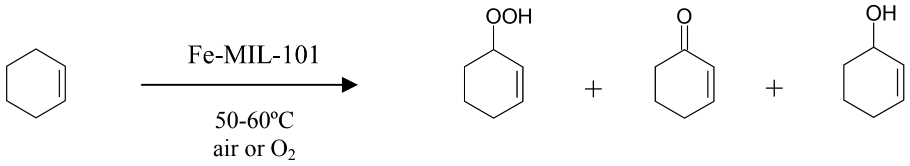

Figure 3. Main products of cyclohexene aerobic oxidation over Fe-MIL-101

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Poster

#1

MATHEMATICAL MODELLING OF THE ADSORPTION-CATALYTIC PROCESSES IN THE MULTI-DISPERSED BED

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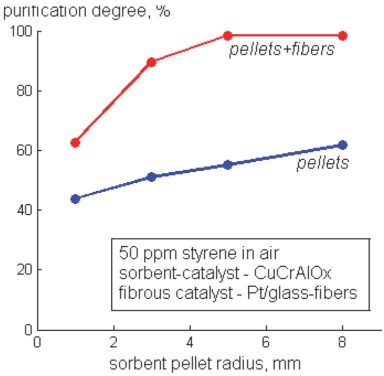
Adsorption-catalytic process for abatement of volatile organic compounds (VOC), including adsorption of VOC at the catalyst surface at ambient temperature with periodical incineration of accumulated VOC at elevated temperature [1-3], is a promising energy-saving technology for purification of lean industrial waste gases. At the same, the purification efficiency of such process may be limited by possible desorption of unoxidized VOC to gas stream during regeneration/incineration procedure [4], therefore, there is the need to develop new technological approaches aimed to minimize such desorption losses.

One of the such approaches is application of the multidispersed adsorption-catalytic packing [5], consisting of comparatively large pellets (say, 5-10 mm) of the catalyst-adsorbent and of catalytically active micro-fibers with typical thickness of ~10 microns [6]. During the heating at the regeneration stage the micro-fiber catalyst will be heated much more rapidly than adsorbent-catalyst, due to the much higher unit outer surface area improving the heat exchange. When the adsorbent-catalyst temperature will become high enough for partial desorption of chemisorbed VOC, the temperature of the micro-fibrous catalyst will be already as high as necessary one for complete oxidation of desorbed VOCs.

This theoretical concept was confirmed by results of the mathematical simulation of combined multi-dispersed system. It was shown, that addition of the microfibrous catalyst leads to significant improvement of the purirfication efficiency of the adsorption-catalytic process.



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#2

MULTICAPILLARY COLUMNS FOR HIGHT SPEED ANALYSIS OF LIGHT HYDROCARBONS AND VOLATILE COMPOUNDS IN GAS CROMATOGRAPHY

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The light hydrocarbons are the important part of oil, natural gas, feedstock for petrochemical synthesis and other petrochemical products. For C1 –C6 hydrocarbons analysis the capillary or packed columns the gas chromatography mode are well known. However the process of separation using columns of these types need a long time of a minute scale. One of the way to achieve a seconds for GC separation are to use the multicapillary columns (MCC). Multicapillary columns consist of the large number (more then 1000) capillaries which work as chromatographic column. Small both length (10-30 cm) and diameter of capillaries (20-40 microns) allow to separate compounds mixtures during the time of 10 - 20 sec.

Until now all the commercially available multicapillary columns have been made with liquid phase that allow them to be only used for gas-liquid chromatography. But light hydrocarbons separation needs the columns for gas-solid chromatography when the porous adsorbent film exists on the capillary wall.

In our laboratory the methods for preparing gas-solid columns with films based on aluminum oxide, silica oxide, porous polymer by adsorbent synthesis was developed. All these methods based on porous material synthesis inside the capillary. The columns prepared enable to separate the different classes of chemical compounds (C1-C6) during 5-10 seconds and can be used at temperature range from 30 to 200°C.

The method of preparation and the applications gas-solid MCC was discussed. The column applications for high-speed separation light hydrocarbons and another compounds such as alcohols, ketones, aldehydes, esters was resulted. The comparison of chromatographic properties, applications of MCC with different adsorbent types and columns chromatographic properties was conducted.

Poster

#3

ROLE OF THE PHASE AND CHEMICAL COMPOSITIONS OF OXIDE SYSTEM MoVTeNb IN THE SELECTIVE OXIDATIVE TRANSFORMATIONS OF PROPANE

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Catalysts MoVTeNbO are reported [1] to be the most efficient catalysts for the ammoxidation of propane to acrylonitrile and oxidation to acrylic acid. The goal of the present work was to develop a reproducible synthesis of catalyst MoVTeNb and to elucidate the role of its phase and chemical compositions in the oxidative transformations of propane. The catalyst was synthesized from aqueous slurry using ammonium heptamolybdate, ammonium metavanadate, telluric acid and niobium oxalate. The prepared slurry was spray-dried at 220°C and heated in an air flow at 320°C during a short period [2] and in He at 600°C for 2h. The propane (amm)oxidation was carried out in the temperature range of 380-420°C using a reaction mixture of 4% C_3H_8, 30% H_2O, 66% air or 5% C_3H_8, 6% NH_3, 89% air.

The mechanism of formation of oxide catalyst MoVTeNb was determined, the composition and the structure of the resulting product were defined at all synthesis stages, the catalyst preparation conditions were optimized.

The slurry contains a four-component heteropoly anion of the Anderson type (HPA), the same as a dry precursor; the HPA decomposed at 320°C yields a XRD amorphous product containing nano-sized particles, related to M1 and M2 phases structurally and chemically; the above particles are crystallized to M1 and M2 phases during the high temperature treatment.

Acrylic acid and acrylonitrile resulted from the intermediate propylene and acrolein. The role of elements of catalyst MoVTeNb was determined for the intermediate stages. The unique of the catalyst is determined by the M1 phase structure, in which the active centers of each stage are combined in the optimal ratio. Maximal activity and selectivity are observed at more than 80% content of M1 of chemical composition $M_1V_{0.3}Te_{0.12-0.14}Nb_{0.10-0.14}$.

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Acknowledgement:

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Poster

#4

THE SUPPORT EFFECT ON BENZENE BENZYLATION OVER IRON-CONTAINING CATALYSTS

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The liquid phase benzylation of benzene and other aromatics by benzyl chloride is of importance for the production of key intermediates for pharmaceutics and fine chemicals. The efforts to develop heterogeneous catalysts instead of traditionally used homogeneous acid catalysts ($FeCl_3$, H_2SO_4, etc.) revealed the promising features of iron oxide or sulfate.

The aim of this topic is to study the support effect (Al_2O_3 or SiO_2) on the catalytic activity of iron-containing supported catalysts prepared using the iron (II) sulfate precursor.

The catalysts were prepared by incipient wetness impregnation of the silica and alumina grain with the solution of iron (II) sulfate followed by subsequent drying and calcination at different temperatures in the 300-700°C interval for 4 hours (denoted as FS400, FA400 etc.), whereas the iron concentration was about 4 wt.%.

It was stated that only sample supported on silica and calcined at 400 °C (FS400) reveals the catalytic activity, whereas other samples, as well as silica and alumina support do not provide the benzylation of benzene after 24 hours of reaction. An FS400 sample ensures 100% conversion of benzyl chloride in the temperature range 25-70°C. Selectivity does not depend on the reaction temperature and is defined mainly by the ratio of the reactants. Mossbauer spectroscopy data let us to suppose, that in the FS400 sample iron is present in the three different position, specific for iron atom in $Fe_2O(SO_4)_2{*}xH_2O$, $FeOHSO_4{*}xH_2O$ and $FeOHSO_4$. It was shown earlier; this compound is transformed to highly dispersed ε-Fe_2O_3 particles (2-5nm) after calcination at the temperature above 700°C. On the contrary, Fe (III) hydroxide is formed on alumina (FA) surface after drying at 110°C. The further calcinations at 500°C led to α-Fe_2O_3 formation. Apparently, the high catalytic activity of FS400 is provided by the complex compound iron containing compounds on the silica surface, containing oxide, hydroxide and sulfate groups as anions. The details of this reaction will be disclosed in the further investigation.

Acknowledgement. The authors acknowledge financial support from RAS Presidium (program № 27, project № 46)

Poster

#5

INSIGHTS INTO THE REACTIVITY OF MIXED COMPOSITES WITH PEROVSKITE STRUCTURE $(LA_{1-Y}SR_Y)_{N+1}(MN,FE)O_{3+N}$ (N=0,1; Y=0-1) IN HIGH TEMPERATURE N_2O DECOMPOSITION AND METHANE COMBUSTION

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Nowadays Sr-substituted $LaMnO_3$ and $LaFeO_3$ are considered as one of the most perspective catalysts for high-temperature catalytic reactions with participation of oxygen. However, the nature of their reactivity remains unclear. Among the most important factors of high reactivity of Sr-substituted manganites and ferrites are:

- enhancement of oxygen mobility in the bulk due to formation of ionic point defects;
- modification of the surface properties (surface oxygen mobility, phase composition) as a result of changes in the microsctructure and morphology of the catalyst particles or surface segregation processes.

In this work we aimed at establishing the relationship between oxygen transport properties, phase composition and microstructure of the catalyst particle and catalytic properties of $La_{1-x}Sr_xMnO_3$ and $La_{1-x}Sr_xFeO_3$ in high-temperature reactions of methane combustion and N_2O decomposition.

Quantitative characteristics of high temperature surface and bulk oxygen mobility both in manganites and ferrites were derived from analysis of the labeled oxygen distribution in the gas phase after stepwise $^{16}O_2/^{18}O_2$ substitution (SSITKA) at 800-900 °C. A correlation between the coefficient oxygen diffusion the bulk ($La_{1-x}Sr_xMnO_3$) or the rate of surface oxygen exchange ($La_{1-x}Sr_xFeO_3$) and catalytic activity was found. It gives us reason to propose a kinetic model considering reactivity of lattice oxygen towards N_2O decomposition and methane combustion.

Detail investigation of the microstructure of the catalyst particles revealed that surface and bulk composition do influence oxygen mobility. It was shown that depending on the nature of Sr precursor the surface segregation of layer-structured perovskite $(La_{1-y}Sr_y)_2Mn(Fe)O_4$, which possesses high surface oxygen mobility, took place. As a consequence, modification of the surface with layer-structured perovskite resulted in high catalytic activity of composite samples.

Poster

#6

STUDY OF ELECTRON AND GEOMETRIC STRUCTURE AND CATALYTIC PROPERTIES OF CuO NANOPOWDERS

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The utilization of carbon monoxide is an important ecological problem because of its high toxicity and huge daily CO emission into the atmosphere. Various systems have been proposed for this process, including copper-containing catalysts, which have comparable activity to catalysts based on noble metals. The low cost of copper-based catalysts is another one important advantage. The investigation of surface oxygen species on model cupric oxide will allow explaining abnormal activity of systems based on nanostructured copper oxide particles.

In the present work copper oxide nanosized powder samples were produced and studied by means of TPR-CO, TPR-H_2, XRD, HR TEM and XPS. For all samples the CuO phase was detected by XRD analysis. Coherent-scattering region was 7-15 nm for all samples. HRTEM showed formation of oblong CuO particles with width about 10-20 nm and length more than 100 nm. Light-off tests demonstrate low temperature activity (LTA) in catalytic CO oxidation for all nano-powder samples. (Fig. 1). All studied by XPS samples contain one main oxygen state with Eb(O1s) = 529.4 eV attributed to CuO lattice oxygen (Figure 1b). In comparison with massive CuO oxide the formation of additional non-lattice oxygen state with Eb(O1s) = 530.9 eV was observed. Non-lattice oxygen state can not be attributed to the Cu2O speciesor to the impurities. The nature of detected non-lattice oxygen is not totally clear – some different explanations are discussed.

Summarizing all experimental data it is possible to conclude that low-temperature CO oxidation is connected with the non-lattice oxygen state forming at the surface of nanostructured CuO.

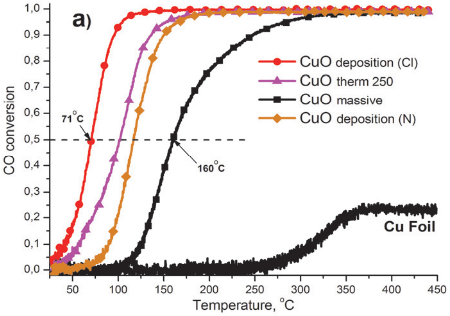

Figure 1. CO conversion vs temperature

Acknowledgment. This work was supported by the Russian Foundation for Basic Research through grant number 10-03-00843-a.

Poster

#7

SOLID SOLUTIONS OF COMPLEX SALTS AS SINGLE-SOURCE PRECURSORS FOR Pd-Pt, Pd-Cu AND Pd-Au NANOALLOYS

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Compounds with identical structure can cocrystallize into single phase solid solution if they have close unit cell parameters. On the ground of this fact we chose the pairs of complex compounds of palladium, platinum and copper, which meet these requirements and also can decompose at relatively low temperatures to yield fine metallic product. The latter condition can be fulfilled by using ligands and counter-ions which consist of light nonmetals (C, H, N, O) and possess marked reductive properties.

In case of Pd–Cu system we prepared solid solution of acetylacetonates $[Cu_{0.67}Pd_{0.33}(Acac)_2]$ by evaporation of mixed chloroform solution. Due to high volatility of these complexes the solid solution was decomposed to bimetallic $Cu_{0.67}Pd_{0.33}$ by thermal shock.

Platinum(II) and palladium(II) have numerous isostructural compounds. By means of joint crystallization or precipitation the next bimetallic solid solutions were obtained: $[M(NH_3)_4](NO_3)_2$, $[M(NH_3)_4](HCO_3)_2$, $[M(NH_3)_4]C_2O_4$ и $(NH_4)_2[M(C_2O_4)_2]\cdot 2H_2O$ ($M = Pt_xPd_{1-x}$, x=0.25, 0.33, 0.5, 0.75). Individual salts and bimetallic phases have been characterized with IR-spectroscopy, elemental, XRD and thermal analysis. Decomposition of mixed complexes in different atmospheres (H_2, He, O_2) was studied. It was shown that thermal behavior of mixed complexes is closer to pure palladium salts.

It is complicated to find isostructural compounds of differently charged palladium(II) and gold(III). Therefore we synthesized double complex salt $[Pd(NH_3)_4][AuCl_4]_2$. It was shown that the phase composition of thermolysis products ($Pd_{0.33}Au_{0.67}$, PdO+Au, Pd+Au) strongly depends on heating rate and nature of atmosphere.

Bimetallic catalytic samples prepared by incipient wetness impregnation of $[Pd_{0.33}M_{0.67}]$ on CeO_2 and subsequent thermal treatment. The products were tested in reaction of low-temperature CO oxidation and investigated with XRD, XPS and HRTEM.

Poster

#8

MICROWAVE-ASSISTED DECOMPOSITION OF ABSORBED HEAVY OILS

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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 [1]. The idea of the present work is to perform cracking of heavy oil residues inside porous granules of a catalyst. A granule of a MW-absorbing porous material is soaked with the oil residues. Thus we form a solid particle which is easily loaded via any kind of reactor and doesn't limit the exchange by gaseous substances with the ambient. Then these particles are heated rapidly to high temperatures by MW, and the volatilized compounds are collected.

In our experiments, we succeeded to obtain a very high rate of the granules heating (about 1000 ^{o}C/min). So, the oil soaked sorbent was heated to 700 ^{o}C in very short period of time. In that conditions, desorption of heavy oils is followed by their thermal decomposition (cracking) with the formation of lighter hydrocarbons. The decomposition degree was about 50% in the case of black oil and 60% in the case of heavy oil. But about 15% of the initially soaked oil stays in the pores of the sorbent and undergo the coke formation. This leads to a reduction of the specific surface of Sibunit from 500 to 300 m^2/g. Note, that in such cases the coking + cracking do not considerably diminish the mobility of the granules which may help a lot at the process design and engineering.

In some experiments zeolite ZSM-5 was added in the reactor. During the MW irradiation, some products of pyrolysis appear to be absorbed by the zeolite, where they underwent a secondary decomposition. That allowed us to increase the overall decomposition degree up to 75% in the case of black oil and 80% in the case of heavy oil. However, the content of coke in the pores of sorbent was unchanged after the reaction.

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