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2011

Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia

Institute of Catalysis and Petroleochemistry, CSIC, Madrid, Spain

International conference

Nanostructured catalysts and catalytic processes for the innovative energetics and sustainable development

Devoted to the Year of Spain in Russia and of Russia in Spain

June 5-8, 2011

ABSTRACTS

Novosibirsk, Russia – 2011

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Financial support

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KEY-NOTE LECTURES

KL-1

R & D ACTIVITIES OF THE INSTITUTE OF CATALYSIS AND PETROLEUM CHEMISTRY (ICP) IN THE FRAME OF THE SPANISH NATIONAL RESEARCH COUNCIL (CSIC)

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The Spanish National Research Council (CSIC), 12.000 staff, is the largest public institution dedicated to research in Spain and the third largest in Europe, and it belongs to the Spanish Ministry of Science and Innovation. CSIC is a multidisciplinary institution that covers practically all fields of knowledge. It is organised in eight scientific areas, among them the one devoted to Chemical Science and Technology, integrated by twelve institutes, and to which ICP belongs.

ICP, established 1975, develops its activities in three main research areas, energy, environment and chemical synthesis, combining both heterogeneous and enzyme catalysis. Its capabilities embrace the development of novel catalytic materials and processes, the design of methodologies for processes control and advanced techniques for catalysts characterization.

ICP has around 200 staff, including 45 researchers with permanent position. Over the last few years, ICP has contributed to 15% of the PhD and papers published in the Chemistry Area of CSIC, and 20% of the patents. Moreover, 7% of the patents belonging to CSIC have been issued by researchers of ICP in 2009.

KL-2

ACTIVITY OF THE INSTITUTE OF HYDROCARBONS PROCESSING SB RAS IN THE FIELD OF NANOSTRUCTURED CATALYSTS

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The lecture consists of two parts. The first part is a brief presentation of the Institute of Hydrocarbons Processing SB RAS, Omsk (IHP), which was founded in 2003 on the basis of Omsk Department of the Boreskov Institute of Catalysis.

Main line of the IHP research activity is studying the mechanisms of chemical transformation of hydrocarbons aimed at the development of advanced catalysts and technologies for chemical processing of oil and gas hydrocarbons into a wide spectrum of products for various applications, in particular, fuels, products of petrochemical and organic synthesis, and functional carbon materials.

Having two large departments of: i) oil refinement and petrochemistry and ii) functional carbon materials, IHP carries out wide-ranging studies, both fundamental and applied, on the entire complex of problems in these areas: from regularities of hydrocarbon conversion reactions and mechanisms of the active sites formation in appropriate catalysts to implementation of some technological stages at big pilot plants. The IHP presentation is concluded with a brief overview of processes under development or already implemented in practice, which are based on nanostructured catalysts created at the Institute.

Second part of the lecture gives a more detailed description of results obtained at IHP on nanostructured platinum-alumina catalysts in the last three years.

1. The formation regularities of polynuclear platinum species fixed on γ-Al_2O_3 and possessing specific adsorption and catalytic properties were determined. Thermal analysis with mass spectrometry, UV-IR spectroscopy, XRD, and X-ray radial electron density distribution spectroscopy were used to reveal changes in the composition and structure of the complex during hydrothermal treatment. The overall data allowed us to propose a structural model of the complex.

Testing of samples synthesized from a hydrolyzed precursor in the transformation of n-heptane showed a higher aromatization selectivity as compared to conventional “chloride” catalysts having a similar activity.

2. A growing demand for C_2-C_4 alkenes intended for the production of polymers underlies the interest in catalytic dehydrogenation and initiates the development of new catalytic systems. Most promising are the catalysts with magnesium aluminum oxides formed from a layered hydroxide precursor like hydrotalcite. Such supports have a moderate and easily controllable basicity, high stability during oxidative regeneration, also they can provide high dispersity of supported

platinum. In this connection, the formation of platinum particles in a layered structure of double hydroxides during the synthesis of Pt/$MgAlO_x$ catalysts was studied. Diffuse reflectance electron spectroscopy, thermal analysis, X-ray diffraction, low-temperature nitrogen adsorption, ^{195}Pt NMR, thermoprogrammed reduction, X-ray photoelectron spectroscopy, and high resolution transmission electron microscopy were used in the work. It was found that fixation of platinum complexes on hydrotalcite with interlayer OH ions increases interplanar spacing and thermostability of the layered structure. In the synthesized Pt/$MgAlO_x$ samples, a considerable part of platinum enters the composition of particles with planar morphology having the extension up to several tens of nanometers and thickness not exceeding 2 nm. Pt/$MgAlO_x$ catalysts are characterized by high selectivity toward methylcyclopentane formation in transformation of n-hexane (200-400°C) and high stability in hydrogenation of olefins.

3. Modification of the oxide surface with organic aluminum salts was suggested as an approach to varying the ratio of alumina surface sites. The choice of a particular organic aluminum salt was shown to be of key importance for such modification due to differences in the interaction of acetate, oxalate and citrate complexes of aluminum with the oxide surface. Aqueous solutions of these aluminum salts were examined by ^{27}Al NMR, and adsorption of oxalate aluminum complexes on the γ-Al_2O_3 surface was studied by IR spectroscopy.

Analysis of IR spectroscopy data demonstrated that modification of the functional coverage of γ-Al_2O_3 surface (impregnation with a solution of aluminum oxalate followed by heat treatment) changes the ratio of the types of surface hydroxyl groups and decreases their total amount. Besides, the amount of weak Lewis acid sites also decreases, which is confirmed by positional isomerization of hexene-1 used as a test reaction. Modification of the support leads to changes in catalytic properties of the Pt/Al_2O_3 system in the transformation of n-hexane: hydrocracking processes are suppressed, whereas selectivity to methylcyclopentane increases.

KL-3

CATALYSIS IN RENEWABLE AND NON-TRADITIONAL ENERGETICS

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There are two evident ways to overcome the expected energy problems of the mankind future. First of all, one should increase the efficiency of the use of conventional energy carriers. The second way is to enlarge utilization of nonexhaustible sources of energy which still do not create the basis of the nowadays energetics. A principal role in all these movements belongs to catalytic technologies.

A traditional way in the application of catalytic technologies in energetics is their use for improving the incineration of conventional or available fuels in various large- or small-scale thermal power plants. However, there are also some not so evident applications of these technologies which may appear to be of a principal interest for the future.

This presentation concerns the existing trends in application of catalytic technologies to (i) production of heat from low-calorific feedstock; (ii) conversion of biomass to high quality fuels; (iii) utilization of nuclear and solar sources of energy, (iv) improvement of the efficiency of the mechanical or electric energy production from the energy of chemical energy carriers, and (v) recovery of medium- or low-potential heat wastes or utilization of some widely available heat-energy sources.

KL-4

STRONG METAL-SUPPORT INTERACTION (SMSI) OBSERVED BY AMBIENT PRESSURE PHOTOEMISSION SPECTROSCOPY (APPES) IN A Ni/CeO_2 SYSTEM

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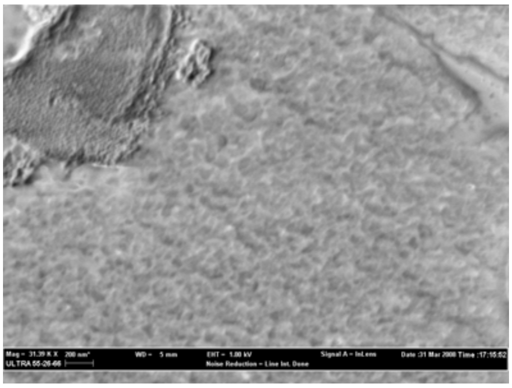
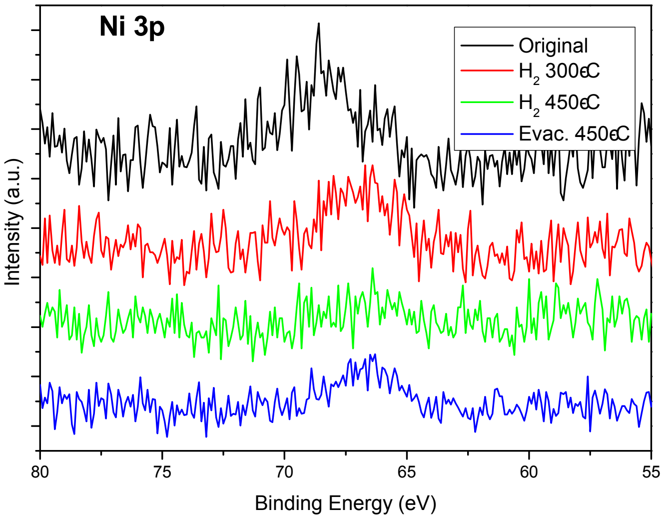


The Strong Metal-Support Interaction (SMSI), an effect characterized by strongly changing the physical and chemical properties of metals dispersed over some reducible oxides as titania and ceria, has attracted scientific interest for more than 20 years [1]. Recently, we have observed this effect in a Ni/ceria powder system [2]. Now, we have studied by APPES the reduction in hydrogen of a model Ni/CeO_2 system (right image). The nickel particles (20nm in diameter) were prepared according to the method described by G.A.Somorjai [3] and were deposited on the ceria support using the Langmuir-Blodgett (LB) method. The support was prepared by an electron beam evaporation method [4]. The evolution of the Ni3p region during the reduction process was examined by APPES spectroscopy (figure below). It shows as the partially oxidized metal particles are reduced to the metallic state upon hydrogen reduction at 300ºC, and almost vanishes upon reduction in hydrogen at 450ºC. Simultaneously, the cerium oxide support is partially reduced to Ce(III). Finally, by evacuating the sample at this high temperature, the Ni signal is almost completely recovered. All these effects, observed in situ for the first time, can be explained considering the mobilization of the metallic and/or the cerium oxide phases associated to the SMSI phenomenon, leading to the decoration and burial of the metallic particles by the reduced cerium oxide.



Thanks are due to the ALS facility and staff, and the Project ENE2007-067926-C02-01

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KL-5

USE OF CO_2 FOR SELECTIVE OXIDATION IN PETROCHEMISTRY

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The oxidative route is a potential alternative to dehydrogenation processes but still shows some disadvantages. Due to its exothermic character in the presence of oxygen, it is necessary to remove heat and due to the strong oxidation ability of O_2, overoxidation of desired products limits the selectivity. Since the pioneering work of Krylov's group[1], the use of carbon dioxide (CO_2) as a mild oxidant is a promising alternative to O_2. Besides being an oxidant, it is non-toxic, strongly reduces the flammability limits and, due to Kyoto Protocol, its economic cost is even negative. Different active and selective catalytic systems have been searched, that can be splitted into two main groups: cerium-based[2,3] and transition metal (Cr, Mn, Fe)[1,4] oxides. Despite the research efforts, the effect of the CO_2 is still unclear. Some authors propose that it is the responsible to generate active oxygen species, some others that it reoxidizes the reduced catalytic species completing the redox cycle[2] and finally others that it oxidizes carbon species reducing coking. However, all these points are still under debate, but it seems clear that the acidity/basicity, redox and oxygen mobility in the catalysts are crucial points to determine the catalytic activity in the oxidative reactions with CO_2.

We report here the reduction and reoxidation of nanostructured ZrO_2-CeO_2 based catalysts doped with variable amounts of Ca. C_2H_4, CO and H_2O are the main products of ethane ODH with CO_2 for all the catalysts. The results of consecutive cycles of hydrogen temperature programmed reduction (H_2-TPR) and CO_2 temperature programmed oxidation (CO_2-TPO) show that these catalysts, easily reduced in H_2 flow, can be reoxided with CO_2. The onset of H_2 and CO_2 uptake was about 350ºC, and 650ºC, respectively. Catalytic activity, tested from 550 ºC to 740 ºC, only reaches >1% conversion at about 680 ºC, which is coherent with the redox mechanism. So, the overall reaction may be described as a result of adding the reduction of the cerium in the catalysts by the ethane: $2\ CeO_2 + C_2H_6 \rightarrow Ce_2O_3 + C_2H_4 + H_2O$ followed by its reoxidation with CO_2: $Ce_2O_3 + CO_2 \rightarrow 2\ CeO_2 + CO$. Similar researches are being conducted on chromium oxide-based catalysts to check the validity of the model for this other catalytic system.

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KL-6

ALKYLATION OF BROWN COALS AND PEAT BY ALCOHOLS

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Alkylation of low-grade metamorphic coals and peat by alcohols in the presence of mineral and organic acids studied with using FTIR, NMR, and GC-MS. The impact of reaction conditions on the yield of extractable matter was experimentally investigated and relevant regression equations were obtained. Changes in the group and individual compositions of the wax fractions of bitumen in the process of brown coal and peat alkylation were studied. It was found that the esters of alkylated coal waxes consisted of the native esters of fatty acids and the alkyl esters of these acids formed as a result of alkylation reaction. Esterification and transesterification were predominant among the reactions of bitumen fraction components. The positive effect of alkylation by alcohol to the increasing of the bitumen yield was found.

KL-7

SYNTHESIS AND PERFORMANCES OF 3-D ORDERED MACROPOROUS MATERIALS

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3-D ordered macroporous materials with the pore sizes ranging from 50 nm to several micrometers are potentially attractive as adsorbents, catalysts, supports and membrane materials. First reports on the methods for manufacturing such materials have appeared in 1997 and concerned inorganic materials patterned on organic templates, such as the equally sized oil-in-formamide emulsion droplets [1] or bacterial multicellular filaments [2]. Later, arrays of monodisperse polymeric spheres began to be used as templates for the synthesis of various inorganic materials, including zeolites, having hierarchical macroporosity structure [3-5].

In our presentation we'll describe results of experiments on the synthesis of 3-D ordered macroporous silica and ZSM-5 zeolite (fig.1), including Fe-containing ones, and their performance in adsorption and oxidation catalytic reactions.

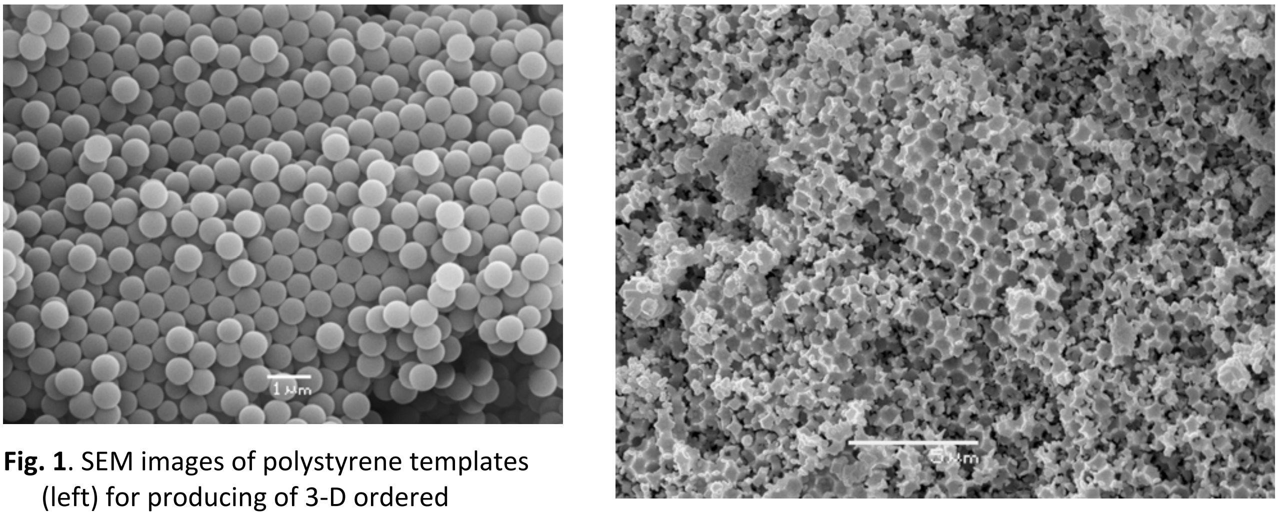

Fig. 1. SEM images of polystyrene templates (left) for producing of 3-D ordered macroporous ZSM-5 zeolite (right).

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KL-8

NEW INTEGRATED CATALYTIC PROCESSES OF WOOD BIOMASS TRANSFORMATION TO PLATFORM CHEMICALS, BIOETHANOL AND LIQUID HYDROCARBONS

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The biorefinery of the future should integrate processes of biomass conversion to fuel and chemicals that are optimized for energy efficiency and resource utilization. The success of biorefinery will require a fundamental understanding of the types of catalytic processes best suited for conversion of main biomass components – carbohydrates and lignin to various chemicals and biofuels. The preliminary fractionation of biomass on individual components opens a new prospects for advanced high-performance biorefinary.

The following methods of wood biomass separation were studied by authors: catalytic oxidation by molecular oxygen in water-alkaline medium to cellulose and aromatic aldehydes; catalytic oxidation by hydrogen peroxide in acetic acid-water medium to cellulose and to low molecular mass lignin (LMML); two-step catalytic hydrolysis to xylose, glucose and hydrolytic lignin; exploded autohydrolysis (short-time cracking by overheated steam) to cellulose, LMML, C_6-sugars, furfural; catalytic cracking by overheated steam to levulinic acid and condensed lignin.

The used methods of wood biomass separation give cellulose, lignin and such platform chemicals as glucose, xylose, levulinic acid, aromatic aldehydes. There are numerous useful compounds derived from these platform chemicals.

The optimal conditions for hardwood (aspen, birch) and softwood (abies, larch) separation on valuable products by studied catalytic methods were selected. On this basis the different ways of integrated processing of wood biomass to chemicals (glucose, xylose, levulinic acid, vanillin, syringaldehyde), bioethanol and liquid hydrocarbons were suggested. Depending on the used method of wood biomass fractionation and type of further transformations of primary products the biorefinary can be directed on dominant production of liquid biofuels or chemicals.

One of the developed processes of integrated transformation of wood biomass to liquid biofuels includes the following steps: catalytic oxidation of wood by hydrogen peroxide to cellulose and LMML, acid-catalysed hydrolysis of cellulose to glucose, fermentation of glucose to bioethanol, thermal conversion of lignin to liquid hydrocarbons in ethanol medium under the pressure. Lignin-based liquid products are enriched by phenols and their alkylated derivatives.

The other example of the developed process of integrated conversions of wood to chemicals is based on the two steps: catalytic oxidation of wood by molecular oxygen to cellulose and aromatic aldehydes (vanillin and syringaldehyde) and acid-catalysed conversion of cellulose to levulinic acid. Aromatic aldehydes, levulinic acid and their derivatives are widely used in food and pharmaceutical industries, medicine, fine organic synthesis and other areas.

KL-9

DESIGN OF CATALYTIC PROCESSES FOR BIOFUELS PRODUCTION

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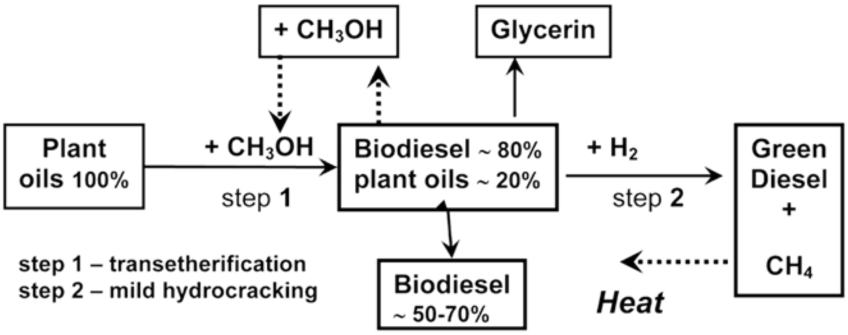
The consumption of petroleum has surged during the 20th century, at least partially because of the rise of the automobile industry. Today, fossil fuels such as coal, oil, and natural gas provide more than three quarters of the world's energy. However at present renewable feedstock attracts attention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

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

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



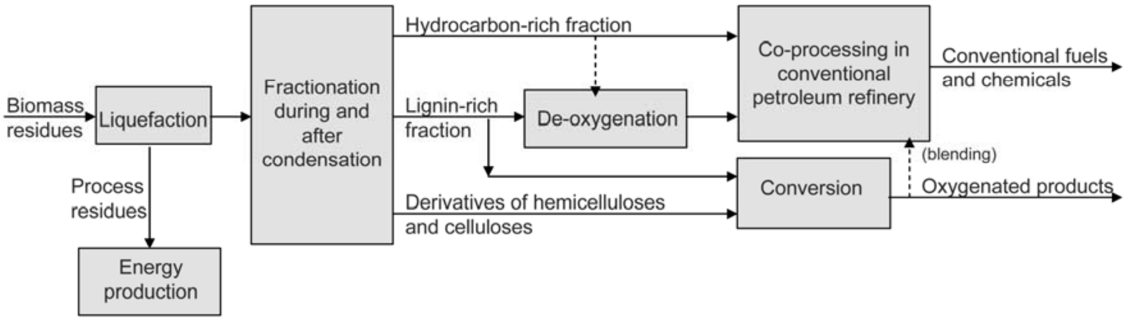
Main features of developed technology are:

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

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

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

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



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

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

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

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KL-10

IMMOBILIZATION-STABILIZATION OF INDUSTRIAL ENZYMES

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Enzymes are able to catalyze the most complex Chemical processes under the most benign experimental and environmental conditions. However, because their biological origin, enzymes have also some characteristics that prevent their industrial implementation. For example enzymes are soluble and generally unstable catalysts.

In this communication a novel protocol for immobilization and stabilization of enzymes is presented. This protocol is based on the multipoint covalent attachment of enzymes on highly activated supports. Now, a number of enzyme residues have to preserve inalterated their relative positions during any conformational change induced by any distorting agent (heat, organic cosolvents, etc.). In this way, thee immobilized should be much more stable than native ones.

Different parameters affecting the multipoint covalent immobilization will be discussed: the morphology of the support, the spacer arm between the enzyme and the support surface, the residues of the enzyme involved in multipoint covalent immobilization, the reactive groups on the support able to promote and intense multipoint covalent attachment, the protocol of immobilization – stabilization, etc.

By using supports activated with glyoxyl groups (small aliphatic aldehydes) reacting with the region of the enzyme surface having the highest amount of lysine residues more than one hundred enzymes have been immobilized and highly stabilized. In general immobilized derivatives preserve 50-80 % of catalytic activity and they were 100-10000-fold more stable than one-point covalently immobilized derivatives. Since, pure immobilization also promotes interesting stabilizing effects, the combination of immobilization inside porous supports plus multipoint covalent attachment may improve the stability of soluble enzymes around or over one million-fold.

KL-11

MICROALGAE BIOMASS AS A SOURCE OF BIOFUELS AND VALUABLE CHEMICALS

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There are currently intensive global research efforts aimed at developing methods for intensive biomass production as a feedstock for commercial biofuels and biochemicals, especially from rapeseed and palm oil. But now it is obvious that above mentioned cultures if used for mass production will compete with traditional farming, and its effectiveness will depend on crop capacity.

It is considered that microalgae offer novel aquatic biomass systems with higher fuel yield potential than traditional cultures and lower water demand than terrestrial biomass, thus will become a promising resource for biofuels production, especially biodiesel. The useful byproduct of biodiesel production is glycerol, which is used as a bulk chemical in production of various substances.

To isolate novel strains of microalgae with expected high biomass production and with high oil yield, we created a method for routine MALDI-TOF mass spectrometry identification of microalgae, thus some prospective strains have been isolated. The main point for developing technology of biofuel production from microalgae biomass is to study physiology of candidate strains and definition of factors influencing their growth and productivity. For that purpose we studied properties of microalga *Botryococcus braunii* UTEX 2441 to define its biomass production process using 110 L flat panel photobioreactor. Due to increase lipids yield this we have started a proteome analysis of *B. braunii* UTEX 2441 proteins during catabolic stage or growth.

Glycerol as a byproduct can be transformed into a number of products, the most important is 1,3-propandiol (1,3-PDO), which is widely used in industry including polymer synthesis and textile coatings with unique properties. We have isolated a number of natural strains producing 1,3-propanediol with high yield. We studied and modified metabolic network of *K. pneumoniae* as a model organism to increase 1,3-propanediol production. Selection of useful features peculiar to industrial strains can be useful for the construction of novel recombinant strains with improved ability to produce the target substance, with high growth rates and resistance to environmental factors.

KL-12

NEW APPROACHES IN VISIBLE PHOTOCATALYSIS FOR ENVIRONMENTAL APPLICATIONS

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Solar photocatalysis is expected to be the ideal green technology for several environmental areas and particularly for a sustainable management of wastes. A visible light photoactive material has been long expected and searched in the last decades. Suitable band engineering is needed in order to develop new photocatalysts for visible light applications[1]. Within this context, the results obtained by our groups can be separated in two different approaches: i) creation of discrete electronic level between the valence and conduction bands, normally achieved by doping or co-doping in the case of oxides[2,3]; ii) the creation of a new valence band by the synthesis of new compounds[4,5].

The extensive structural/electronic analysis carried out suggests that the existence of highly homogeneous Ti–M mixed oxides with electronic properties exclusively leading to a decrease of the band gap would drive to efficient photocatalysts under visible-light excitation. In our case, this occurs with V and W; the low solubility limit of V limits its usefulness and would lead to the conclusion that, within our preparation method, W is the optimum choice to produce Ti-based mixed oxides with photocatalytic activity under sunlight-type excitation.

Regarding to the new systems, the particular junction in the proposed Bi_2WO_6-TiO_2heterostructure will able an optimized charge separation diminishing the recombination process. From the data showed, it might be envisaged an enhanced charge carrier dynamic performed by the conjunction of TiO_2 and Bi_2WO_6. A synergetic mechanism is proposed in which the photocatalyst would efficiently exploit the wide range of the UV and visible irradiation.

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KL-13

DEVELOPMENT OF PHOTOCATALYTIC PROCESSES FOR OXIDATION AND HYDROGEN PRODUCTION

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Sustainable development of modern society requires utilization of renewable energetic and material resources in place of current widespread use of exhaustible fossil fuels and raw materials. Solar light is practically inexhaustible energetic resource for the following several centuries. The solar light energy can be used for carrying out needed chemical reactions and transformed into chemical energy of fuels such as hydrogen.

Titanium dioxide photocatalyst is a thoroughly studied and very active photocatalyst for deep oxidation. It is applied successfully for destruction of organic and inorganic air pollutants. The drawback of TiO_2 photocatalysis is a low energetic efficiency. Our research has shown that combining photocatalysis with non-thermal plasma created in atmospheric electric discharges can increase energetic efficiency of air purification significantly.

Photocatalytic oxidation over cadmium sulfide can be used for highly selective partial oxidation of organic compounds. Our research has demonstrated the first example of selective gas phase oxidation of alcohols into aldehyde and ketone under visible light with oxygen of air. The process can be further developed for green solar organic synthesis.

Hydrogen is a chemical fuel and valuable raw material for chemical industry. It can be produced from water using photocatalytic processes. The common problem of photocatalytic water splitting is separation of its products such as H_2, O_2, CO_2 etc. The available solution of this problem is to separate the oxidation and reduction centers like it is done in plants' photosynthesis. We develop an approach based on porous polymer membrane technology. The TiO_2 photocatalyst is incorporated inside the membrane with the hydrogen production photocatalyst residing on its surface. The three-phase solid-liquid-gas boundary is realized and beneficial for higher rate of photoreaction as compared to suspension systems. The future development of this approach is dreamed to lead to widespread and cheap solar hydrogen production systems that are especially welcomed in unpopulated areas such as deserts and tundra.

KL-14

PREPARATION OF NANOSTRUCTURED GOLD-BASED CATALYSTS FOR ENVIRONMENTAL PROTECTION AND CHEMICAL PRODUCTION FROM THE RENEWABLE SOURCES

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It is well known since 1990-s that metallic gold, when dispersed on various supports in the form of particles with a size of several nanometers, may exhibit extraordinary high catalytic activity and/or unusual selectivity in numerous reactions. The perspectives of gold-containing catalysts to be applied for indoor air-quality and industrial pollution control, fine organic synthesis, PEM fuel cells as fuel cell electrodes, *etc* are extensively studied in many countries.

This report presents recent results of the investigations of gold catalysts, which have been carried out in Surface Science Laboratory at BIC (Boreskov Institute of Catalysis) in collaboration with other laboratories of the institute. The authors have developed and tested different procedures for preparation of the Au nanoparticles supported on alumina and carbon. These supports were chosen from the practical point of view. The changes in the chemical state and local environment of gold during the preparation of the finely dispersed gold particles in Au/Al_2O_3 and Au/C catalysts were studied by a number of physical methods including XRD, TEM, XPS, XAFS *etc*. The epitaxial interaction between Au crystallites and alumina surface, which might be responsible for unexpectedly high resistance of the supported gold nanoparticles against sintering, has been detected.

The Au/Al_2O_3 catalysts show much higher efficiency and stability in the abatement of CO from air and diesel exhausts, as compared to the commercial palladium- and platinum-based catalysts. Gold and palladium-gold catalysts prepared at the BIC also exhibited the high activity and selectivity in oxidation of aldo-sugars such as glucose and lactose into the corresponding polyoxoacids, allowing them to compete successfully with the catalysts based on other noble metals. Finally, nanosized gold particles were first discovered to catalyze the skeletal rearrangement of α-pinene into camphene, which is a key step in the industrial synthesis of camphor from turpentine.

KL-15

ELECTROCATALYSTS FOR PEM FUELS CELLS BASED ON NANOSTRUCTURED CARBON SUPPORTS

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Among the different types of fuel cells, polymer electrolyte fuel cells (PEMFCs and DAFCs) are the most promising for both portable and stationary applications due to its advantageous features such as high power density at lower temperatures (55–95 ºC), low weight, compactness, and suitability for discontinuous operation [1]. At present, the most effective fuel cell catalysts, both in cathode and anode, are highly dispersed platinum-based nanoparticles. The high cost of noble metals used as electrode catalysts is one of the significant obstacles for the commercialization of PEMFCs. Therefore, the metal nanoparticles are normally supported on carbon materials in order to maximize their surface area and decrease the total amount of metal employed. Thus, the fraction of metal particles exposed to the reactants increases, improving the catalysts utilization [2]. Among other factors, the performance of metal nanoparticles supported on carbon materials depends strongly on the properties of the support.

Different carbon materials with high electrical conductivity have been studied as electrocatalyst support for direct alcohol fuel cells (DAFCs) in order to establish their influence on the catalyst properties and to improve their efficiency and stability in the fuel cell. Carbon nanofibers (CNFs), carbon nanocoils (CNCs) and ordered mesoporous carbons (gCMK-3) have been used for synthesizing platinum catalysts by the alcohol reduction process (ethylene glycol, EG). Results have been compared with those obtained for a platinum catalyst supported on Vulcan XC-72R (commercial support) prepared by the same method and for the commercial Pt/C catalyst from E-TEK. It has been demonstrated that novel carbon supports could help to oxidise CO adsorbed on platinum particles more easily than the commercial carbon support, Vulcan XC-72(R) and thus, improve the electrochemical behaviour of the electrocatalysts in the oxidation of alcohols.

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KL-16

COPPER-CERIA CATALYSTS FOR PROX AND WGS PROCESSES IN H_2 PRODUCTION

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CuO/CeO_2 catalysts are active and selective in the mild temperature preferential oxidation of CO by O_2 in presence of H_2 (PROX process), and have been proposed also for the water gas shift reaction (WGS). In previous works of ours[1], of which an overview will be given, the active species in this system have been found by several experimental techniques to be formed by partially reduced CuO clusters dispersed on the ceria surface. Trying to influence the catalytic properties by tuning the $CuO-CeO_2$ interfacial interaction, CuO (1% by weight) has been deposited on different ceria supports which expose different crystal planes of the CeO_2 lattice. Already without CuO, nanocube-shaped CeO_2 exposing mostly (100) faces shows in the $CO+O_2$ reaction higher rate per surface area than other CeO_2 preparations, while stabilizing different surface carbonate species and OH groups as shown by DRIFTS.

CuO/CeO_2 catalysts also evidence different PROX chemistry in both DRIFT spectra and reaction products analysis. Cu^+-CO carbonyls are detected in higher amounts on the ceria nanocube-supported sample, in spite of the lower CuO dispersion expected in this sample due to its lower S_{BET} area. Thus the ceria (100) surface stabilizes higher CuO dispersion or/and higher surface density of Cu^+ species. This sample has lower PROX activity than the other catalysts, may be due to its lower S_{BET}, questioning previous interpretations on the direct relationship between activity and amount of Cu^+-CO species. However, if contact times are adjusted to give at the same temperature (130 ºC and above) a similar CO conversion (≥90%) the nanocube-supported catalyst gives clearly better selectivity (i.e. it oxidizes less H_2) than the other more active catalyst. This evidences again that different chemical reactivity patterns are displayed when the type of surface exposed by the ceria support is different.

Efforts to better understand these systems with other physicochemical studies have been undertaken. On the one hand, quantum calculations at the DFT+U level are carried out on periodic models of the surfaces and of the supported CuO clusters, determining the most stable CuO surfaces and concluding that the formation of O vacancies and adsorbed CO species on them are modified by interaction with the underlying CeO_2. Also, AFM studies of CuO species dispersed on nanocube-shaped ceria have been started.

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KL-17

MODIFIED CERIA-BASED CATALYSTS OF RED-OX REACTIONS: SYNTHESIS AND PERFORMANCE

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This work overviews results of detailed studies aimed at design of ceria-containing catalysts of natural gas and biofuels transformation into syngas and elucidating main factors controlling their performance. As basic systems, nanocrystalline Ln–Ce- $O_{2-\delta}$, Ln–Ce-Zr-$O_{2-\delta}$ (Ln=La, Sm, Gd, Pr) oxides prepared via Pechini route and loaded with Pt, Pd, Ru, Ni, La(Pt)NiO_3 etc were used. The real structure of these systems was studied by TEM with EDX, neutron and X-ray diffraction, EXAFS, Raman, FTIRS of lattice modes. Surface properties were studied by XPS and FTIRS of adsorbed CO. Oxygen bonding strength, mobility and reactivity were characterized by microcalorimetry, O_2 TPD, oxygen isotope exchange, isothermal and temperature-programmed reduction by H_2 and CH_4. Catalytic activity was studied in reactions of CH_4 , ethanol and acetone partial oxidation, steam and dry reforming for both fractions and thin layers supported on ceramic or metal substrates.

Oxygen mobility was shown to be controlled by rearrangement of coordination spheres of Ce (Zr) cations caused by association of dopants with oxygen vacancies; lattice expansion; segregation/clustering of dopants at interfaces, incorporation of supported metals as cationic species into the surface layers of oxides generating oxygen vacancies.

For ceria-based catalysts with a high lattice oxygen mobility, transformation of fuels into syngas proceeds via bifunctional mechanism with fuel molecules activation on metal sites, oxidants activation on oxide sites followed by the surface diffusion of oxygen-containing species to metal/support interface where they transform CH_xO_y species into syngas. Hence, catalytic activity depends on the oxygen mobility in fluorite-like oxides (controlled by the type and content of Ln dopant), metal-support interaction (stabilizes small partially oxidized metallic clusters and results in metal particles decoration by oxidic fragments of support) and metal/alloy particles size and composition (controls efficiency of fuel activation and carbon nucleation). High and stable performance of monolithic catalysts operating with real feeds is achieved without coking provided supported metal/alloy particles size/composition and oxygen mobility are optimized.

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KL-18

NANOCATALYSTS FOR OXIDATIVE WASTEWATER TREATMENT

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The processes of catalytic oxidative destruction of organic pollutants by hydrogen peroxide (catalytic wet peroxide oxidation (CWPO)) and air oxygen (catalytic wet air oxidation (CWAO)) are widely used for wastewater treatment [1,2]. Oxides and mixed oxides of transition metals (usually Cu, Fe, Mn, Co) or oxides supported on stable carriers are often utilized as solid catalysts for CWPO [1]. Two groups of the solid catalysts are used for CWAO. 1. The same transition metals oxides and mixed and/or supported oxides [4,5]. These catalysts are sufficiently effective but they are not stable to leaching of active component into the reaction medium. 2. Nanosized noble metals supported on oxides or carbon. These catalysts are usually stable but much more expensive [5].

The results of systematic research aimed at the development of active, stable and economically effective catalysts for CWPO and CWAO will be reported. Cu- and Fe-containing zeolites, pure carbon nanomaterials and Fe&C composites were investigated as catalysts for CWPO. In CWAO we tested pure nanocarbons and Ru/C catalysts. The correlations between the catalyst morphology, active sites structure, electronic state and dispersion of active metal and catalytic performances as well as catalysts stability were investigated. The kinetic regularities and the mechanism of the processes were also under examination. Such complex research allowed us to propose the active and stable catalysts for each oxidative process.

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KL-19

POLYOLEFINS CATALYST DESIGN BASED ON ANCHORING EARLY-LATE BINUCLEAR SINGLE-SITE SYSTEMS

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Combination of two or more single-site polymerization catalysts in the same reactor is a versatile strategy that multiplies the value of ethylene polymerization catalysts. Such multi-catalytic systems provide access to a wide variety of materials, including composite materials composes of intimate mixtures of different polymers, if the catalysts perform independently, or branched polymer architectures resulting from cooperative interactions between both catalytic centers. Implications of this concept are far-reaching and the full development of its potential is far of being accomplished. This is one of the most challenging and technologically relevant fields in the area of olefin polymerization.

One of the most exciting examples of multicatalytic polymerization catalysts are dual systems composed by “classic” metallocene and late transition metal “postmetallocene” catalysts, e. g. iron bis(imino)pyridine (PDI) complexes. This approach combines the different properties of the individual catalysts, to produce polymer formulations that are uniquely adapted to specific applications. (Figure 1).

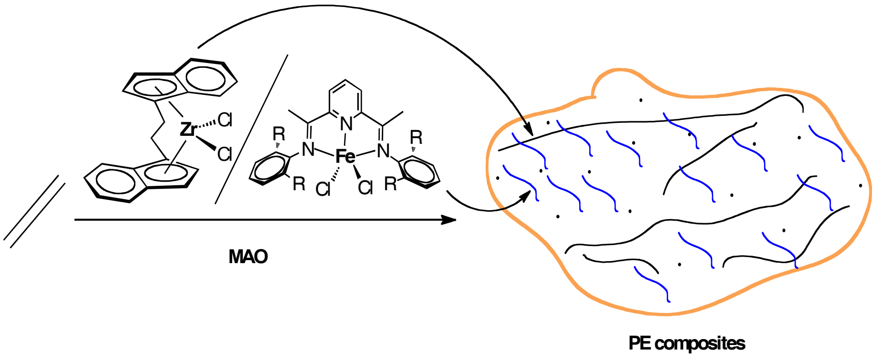

Figure 1

We have recently described that direct synthetic methodology for the synthesis of PDI ligands functionalized at the pyridine ring is feasible. Based on the ability of Manganese(II) organometallics to selectively transfer an alkyl chain to position 4 of the pyridine ring, we found that our method could be ideally suited for tethering the PDI ligand to a variety of molecular

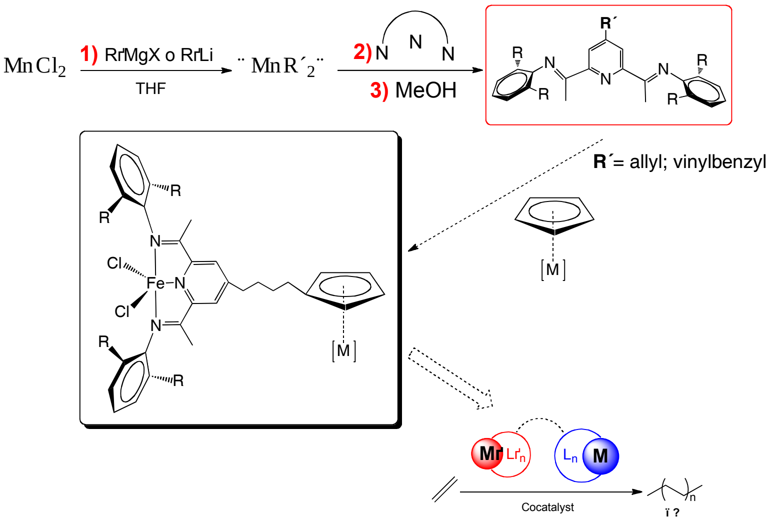

Figure 2.

fragments, including other molecular catalysts. This contribution will describes how this methodology can be exploited and one of our first choices: the synthesis of bimetallic catalysts containing a metallocene unit and an iron-PDI fragment, We believe that properties of these bimetallic systems can be tuned to achieve cooperative integration of the two active centers within a single molecular unit (Figure 2).

KL-20

IMPROVED SYNTHESIS OF SAPO-34 SILICOALUMINOPHOSPHATES FOR THE METHANOL TO OLEFINS (MTO) PROCESS

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The increasing demand of light olefins has renewed the interest of the methanol-to-olefins (MTO) process as a route to obtain these valuable petrochemicals from carbon sources alternative to petroleum. Small-pore silicoaluminophosphates SAPO-34 (CHA) and SAPO-18 (AEI) have been proven efficient catalysts for the MTO process, showing exceptionally high selectivity to lower olefins [1]. However, these catalysts undergo rapid deactivation due to deposition of high molecular weight hydrocarbons on the pore entrances [2,3].

In the present work, we have tried to improve the life time of SAPO-34 catalysts modifying the synthesis procedure by several procedures: (1) by using different templates in order to modify the chemical and physical properties of the catalysts, (2) generating mesoporosity in the crystals by adding different mesoporogen additives, in order to avoid the rapid deactivation observed in the conventional catalysts and comparing different synthesis methods trying to decrease the crystal size of the materials which, as we have seen, is a very important parameter to improve the life time of the catalyst [6].

All the samples have been characterized by different physicochemical techniques (XRD, SEM, N2 adsorption, FTIR, TGA, NMR, chemical analysis), and the catalysts have been tested in the reaction of methanol to olefins, in a fixed-bed reactor at atmospheric pressure and 723 K. The catalysts were pre-treated in a N2 flow at 723 K for 1 h. The reaction products were analyzed on-line by gas chromatography.

Samples synthesized with tetraethylammonium hydroxide (TEAOH) as structure directing agent possessed smaller crystals and showed better catalytic performance. It has also been observed that increasing the mesoporosity and decreasing the crystal size down to the nano scale, it is possible to increase the life time of the TEAOH-SAPO-34 catalysts in more than three times.

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KL-21

SYNTHESIS OF PROPYLENE GLYCOL METHYL ETHER FROM METHANOL AND PROPYLENE OXIDE OVER Al, Al,Zr- AND Zr-PILLARED MONTMORILLONITES

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Glycol ether is widely used as an industrial solvent for coating material and printing inks. Propylene glycol ether is expected to be a safe substitute for toxic ethylene glycol ether due to the negligible toxicity. The propylene oxide route is the most convenient and the most industrially feasible. The attempt to heterogenization homogeneous catalyst as alternatives to traditional catalysts is one area of research which provokes increasing interest.

Catalysts based on clay minerals possess unique structural and catalytic properties due to the capacity adjustable of surface acidity and nature of cation. Al-, Zr- and mixed Al,Zr-pillared interlayered clays (Al_xZr_y-PILC) have been synthesized by the exchange reaction between Na-containing naturally occurring montmorillonite and Al-, Zr- and mixed Al,Zr-cation solutions [1, 2]. The obtained Al_xZr_y-PILCs were characterized by far FT-IR and DR-UV-vis spectroscopy, EPR, ^{27}Al NMR, scanning electron microscopy and N_2 adsorption. Acidity of Al_xZr_y-PILC was studied by Hammett acidity titration with n-butylamine and FT-IR spectroscopy using pyridine, PhCN and $CDCl_3$ as probe molecules. It was shown that the nature of pillaring agent determines texture characteristics and surface acidity of Al_xZr_y-PILCs.

The relationship between the acid-base properties and catalytic performances of Al_xZr_y-PILCs was revealed in the synthesis of propylene glycol methyl ether from methanol and propylene oxide. It was shown that the increase in Al content due to the prolonged of the aging time of Al-hydroxypolycation pillaring solution favours the increase in the activity of Al-PILCs. The conversion of propylene oxide and the selectivity to 1-methoxy-2-propanol decrease with increasing the amount of zirconium in Al_xZr_y-PILCs due to the change in acid-base properties.

Headings: **Structured catalysts for chemical processing and environmental protection**

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KL-22

NEW DEVELOPMENTS IN THE AREA OF NONSTATIONARY AND SORPTION-ENHANCED CATALYTIC PROCESSES

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The presentationis dedicated to catalytic processes performed under artificially created catalystnonstationarity. It is shown that the highest technological effect can be achieved for acontrolled combination of the thermal nonstationarity with the composition nonstationarity ofthe catalyst surface.

Prospective for application of unsteady catalytic and sorption-catalytic processes areanalyzed for different case applications:

- VOC incineration
- NOx reduction,
- purification of automotive exhausts,
- Claus process and H_2S decomposition,
- SO_2 oxidation,
- hydrogen production by steam conversion of hydrocarbons and organic feedsctock,
- selective anaerobic oxidation of hydrocarbons and others.

The following advantages of the sorption-catalytic technologies over the stationarymethods can be mentioned:

- principally new options for heat management, possibility to perform highly-exothermalreactions in packed adiabatic beds without catalyst overheating;
- a decrease in the energy consumption in processing of lean waste gases;
- an increase in the efficiency of cleaning of exhaust gases;
- the shift of equilibrium in thermodynamically limited reactions;
- the enhanced selectivity of partial «anaerobic» oxidation processes using thechemisorbed oxygen as a «soft» oxidant.

In many cases, these advantages may include the reduction in the capital costs in and also, paradox at the first glance, the simplification of technological schemes andthe enhancement of their operation stability.

In general, unsteady state and sorption-catalytic ideology discovers new degrees offreedom for process development and may become the basement for new generation ofhighly-efficient catalytic technologies in the nearest future.

KL-23

OXIDATIVE DEHYDROGENATION OF PROPANE IN MEMBRANE REACTOR: THEORETICAL PREDICTIONS AND CATALYTIC EXPERIMENTS

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Light olefins are important chemicals in synthesis processes because of their high chemical activity in certain reactions. Propylene, one of the most valuable petrochemicals, is nowadays produced either by steam cracking of liquid feedstocks or is recovered from off-gases produced in fluid catalytic cracking units in refineries. The remainder of propylene is produced via on-purpose technologies such as propane dehydrogenation and metathesis [1]. These processes suffer from thermodynamic limitations, coke formation and require costly heat exchange at high operating temperatures because of the endothermicity of the reaction.

While the propane conversion may be increased by operating at higher temperatures, these results induce an increase in the rate of catalyst deactivation and a decrease in the reaction selectivity for propylene. In the last several decades, inorganic catalytic membrane reactors (CMR) have attracted extensive attention in the research community [2]. The use of a membrane allows one to selectively remove a product from a reaction that is limited by chemical equilibrium, shifting the reaction towards the product side and simplifying subsequent product separations. Propane dehydrogenation in a hydrogen permselective membrane reactor may be a potential method for increasing conversion while maintaining acceptable catalyst deactivation rate and reaction selectivity [3]. The oxidative dehydrogenation of propane proposed as a good alternative to traditional propylene production processes was also studied in membrane reactors: in the work [4], the porous catalytic membrane (V–Mg–O) was used.

In our theoretical study we have simulated the “conjugated” propane dehydrogenation in the fixed bed membrane reactor to determine the optimal membrane properties including permeability. From other hand we have applied the aerogel technique to produce ultra active VO_x*MgO oxide system which seems to be very promising for further use in the CMR.

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KL-24

DIFFERENT FLOW METHODS FOR ACCURATE COMPARISON OF CATALYTIC ACTIVITY OF HETEROGENEOUS CATALYSTS

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The catalytic activity is a major aspect of catalytic performance. The accurate measurement of experimental data in a laboratory reactor is very important for preliminary screening or kinetic investigation of the catalysts. There are two related points of activity test strategy. What are we going to measure and how are we going to do it? The choice of the lab-scale reactor determines values that can be measured. However, not all characteristics obtained can be used as criterion of the catalytic activity. Inaccurate comparison of the catalytic activity leads to wrong conclusions.

In this work we analyze plug-flow and gradientless modes which can be used for investigation of steady state catalytic performance.

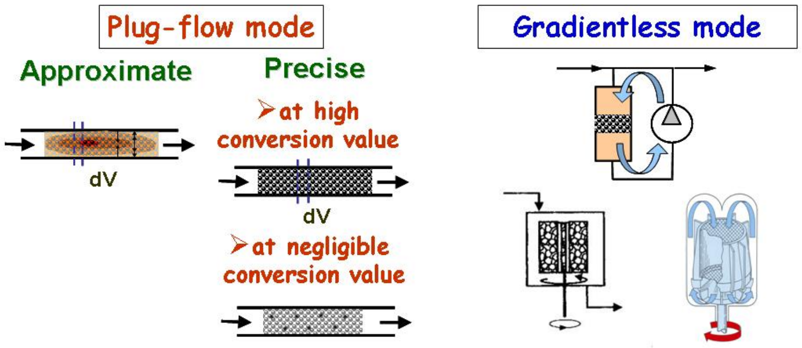

Figure 1. Different types of flow methods

Advantages and disadvantages of these modes are considered. For example, when we want to realize the precise plug-flow mode in lab-scale reactor we should take into account possible temperature and concentration gradients in the catalyst layers. Moreover, even the precise plug-flow mode with the high conversion values cannot be used for correct and objective comparison of catalysts with different mass, area of active component or number of active sites. In order to compare the catalytic activity of different catalysts correctly and objectively we should compare specific stationary rates of catalytic reaction at certain temperature, pressure, and composition of the reaction mixture being in contact with the catalyst surface. The plug-flow mode at the negligible conversion values and the gradientless mode allow measuring one.

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KL-25

MULTICAPILLARY COLUMNS FOR HIGH-SPEED GAS CHROMATOGRAPHY

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Everybody who apply chromatography in daily activity, well know the long and sometimes weary period after probe injection till the separation result appearance.

At present an application a capillary batch as a high speed chromatographic column is one of the ways of analysis time decrease.

However, practical application of capillaries bundle became feasible only after the development of technology of manufacturing the multicapillary rods with a narrow distribution of the capillaries radius. This distribution appears to be highly important parameter of multichannel tubes which are used in preparation of multicapillary chromatographic columns (MCC). Another important point in MCC technology is a loading of chromatographic material (stationary phase) on capillary wall. MCC provide good opportunities in a sufficient acceleration of the reliable gas chromatography via reducing the separation time in the gas-liquid and gas-solid chromatography. The columns allow a successful combination of both the high-speed properties of narrow bore capillary columns and a relatively large amount of the sample to be analyzed.

MCC in gas gas-liquid mode (with polysiloxane liquid phases) with the efficiency of 4000-6000 theor. plates at length 22 cm are acceptable for solving a wide scope of problems requiring a rapid analysis. Note as well that for the majority of practical tasks, one should not use long multicapillary columns, since the length increases the analysis time, while in some cases the elution time may appear to be a more important parameter than the column efficiency.

The columns for gas-solid GC for light based on adsorbent films of alumina and silica oxides or organic porous polymer film of divinylbenzene-styrene. The columns prepared enable to separate the different classes of chemical compounds (C1-C6), light hydrocarbons during 5-10 seconds with efficiency 2000-2200 theor.plates and can be used at temperature range from 30 to 200°C.

The columns preparation methods, column properties and application in different areas of chemistry are discussed.

KL-26

HYDROGEN PRODUCTION IN MICROCHANNEL REACTORS

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Process intensification occurs whenever one enhances mass/heat transfer and reaction rate. Microreactors are devices to carry out chemical reactions having at least one dimension smaller than 1 mm in which process intensification takes place since both mass and heat transfer may be intensified. The widespread use of portable electric and electronic devices increases the need for efficient autonomous power supplies that replace the currently predominant battery technology. The use of common fuels/chemicals, such as hydrocarbons or alcohols, as an energy source is a promising alternative when combined with the recent developments in microchannel reactor technology. Here we report some results of our research project "Integration of Microchannel Catalytic Reactors for Hydrogen Production from Alcohols"[1] emphasizing the design and testing of microchannel reactors for the cleanup process since an essential requirement for the reformate-fed PEMFC is the removal of CO from the H_2 stream after the reforming and water–gas shift reactions.

The synthesis of the catalyst, the manufacturing and coating of the microchannel reactor are summarized, figure 1. In addition the catalytic performance of the microreactor during the CO-PROX reaction is presented, analyzing the effect of the catalyst activation prior to the reaction and the influence of the presence of H_2O and CO_2 in the feed-stream. Finally the experimental results of the CO conversion and O_2 selectivity are compared with the simulations using a model previously formulated.

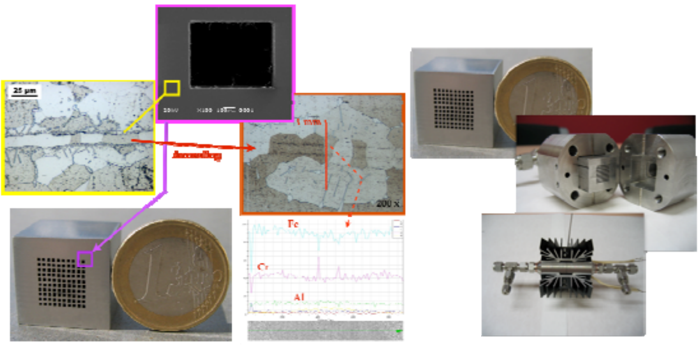

Figure 1. Different steps in the manufacture of a CO-PROX microchannel reactor

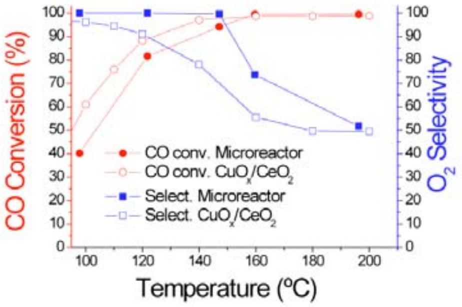

Figure 2. Activity and Selectivity in the microreactor, coated with an active CuO_x/CeO_2 catalyst .

A microreactor, coated with an active CuO_x/CeO_2 catalyst was successfully tested on the CO-PROX reaction under a simulated reformate off-gas feed. Prior to the reactions, the catalysts were activated under O_2 or H_2 with no significant differences in activity, obtaining a maximum CO conversion at around 200 ºC, figure 2. As regards the O_2 selectivity, the results allowed confirming that the CO conversion is thermodynamically favored against H_2 oxidation at low temperatures. On the other hand, it is found that the presence of CO_2 in the feed inhibits the CO conversion at low temperatures, probably by the formation of carbonyl species at the catalyst surface.

Finally, a CFD model developed for a microreactor was successfully validated for the first time with experimental catalytic results. The kinetic scheme previously formulated for the CuO_x/CeO_2 powder catalyst was also corroborated.

[1] Project carried out by Inst. of Material Sciences of Seville, U. of Seville-CSIC, Seville, Spain; Dept. Appl. Chemistry, Universitiy of the Basque Country, San Sebastián, Spain; Public University of Navarra, Pamplona, Spain; and Inst. Catalysis, CSIC, Madrid, Spain

KL-27

CATALYTIC COATING OF METALLIC MONOLITHS AND MICROCHANNEL REACTORS

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During last decade, catalysts on metallic surfaces are reaching a prime importance. Two types of structures justify this interest: metallic honeycombs and microchannel reactors. Metallic honeycombs (monoliths) is the best option for processes where pressure drop and thermal and mechanical resistance are key issues. On the other part, microchannel reactors are in the nucleus of the new tendency to process intensification.

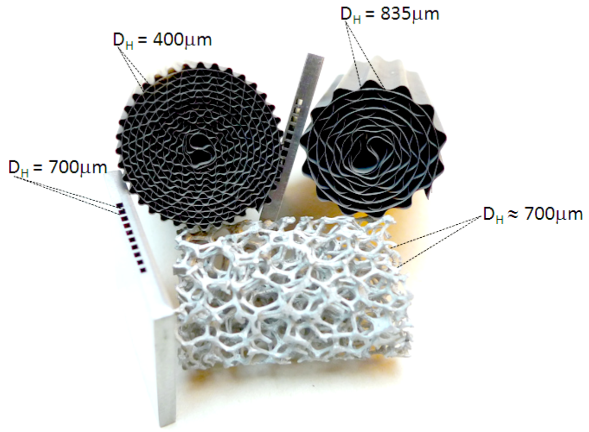
For the preparation of structured catalysts and reactors based on metals, the main step is to produce the catalyst coating on the metallic surface with the required characteristics: amount, homogeneity and adhesion. Different techniques have been proposed to coat metallic structures, like in situ growing, electro-deposition, anodisation, CVD, PVD…etc. But the most popular and versatile is washcoating or dip coating. With this technique homogeneity, amount and adhesion can be obtained on most metallic surfaces controlling the metallic surface properties (depending on the alloy composition and pre-treatment conditions), the coating procedure including the excess elimination, and in particular the properties of the catalyst slurry.

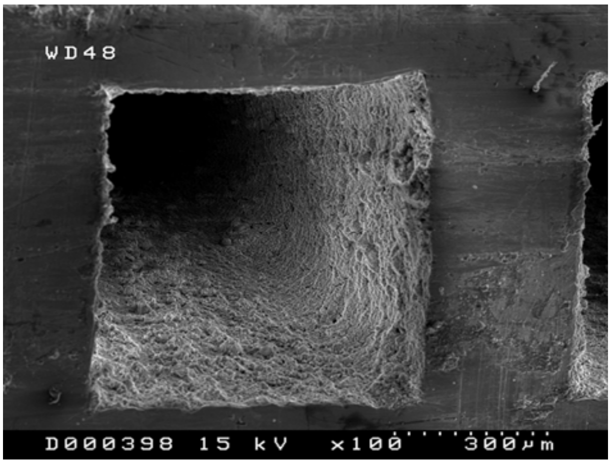
This communication review the main parameters controlling the catalytic coating of metallic monoliths and microchannel reactors by anodization, in situ synthesis and washcoating, based on the experience in our laboratories studying different systems: catalysts for VOC elimination, Fischer-Tropsch synthesis, methane, methanol and ethanol reforming, WGS and PROX. For every reaction several catalysts have been tested on different alloys: Fecral, AISI 304, Brass and aluminium.

Between the variables studied the most relevant are:

- The metallic substrate interface that is produced by an adequate pre-treatment producing a protective scale that must be adherent, chemically compatible with the catalytic coating and offering a high roughness to facilitate a mechanical anchoring.
- The anodization parameters, current density, electrolyte, temperature…
- The elimination of the slurry excess after the washcoating procedure to assure a thick homogenous film but preventing the channel blocking.
- The slurry properties, in particular viscosity and wetting of the substrate (contact angle). These properties depend mainly on the catalyst particle size, solid content and additives.
- Nature and content of the additives. Two types of additives are used to stabilize the slurries, modulate the viscosity and promote adhesion: organic additives like polyvinyl alcohol, PMMA, PVP… that disappears after calcination, and inorganic colloids like alumina, silica, ceria… that remains on the final catalytic coating.

When this group of variables are fitted, it is possible to obtain homogenous coatings presenting adherence higher than 90%, and loads from 0.5 to 5 mg/cm^2 that depending on the coating density means thickness of around 2 to 50 µm.





KL-28

ELECTRON SPIN RESONANCE FOR CATALYSIS. FROM SUPPORTED NANOPARTICLES TO PARAMAGNETIC CLUSTERS IN SUPERCRITICAL FLUIDS

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The application of ferromagnetic resonance (FMR) in chemistry, in particular, in catalysis is rather limited. Largely this is due to fundamental difficulties that arise in the investigation of the electronic system with strong exchange interaction. Magnetic order is the property of volume, while the majority interest of catalytic reactions occur on the surface. The broadening of the absorption lines typical for FMR reduces the resolution of the method and leads to its low information capability. A variety of interactions that determine the absorption characteristics of exchange coupled systems, impede the interpretation of the resonance spectra. Moreover in the real systems the situation is also complicating the magnetic interparticle interaction. All these difficulties would seem to make it impossible to use the FMR for the study of catalytic systems.

The situation changes radically when it comes to nanoscale systems that are of particular interest for catalysis. With decreasing particle size magnetic anisotropy energy decreases. At a certain size, thermal fluctuations of the magnetic moment leads to the so-called superparamagnetic behavior, reflected in an effective narrowing of the observed resonance lines. In this case, due to the high percentage of surface atoms, the use of FMR allows us to study the adsorption, the interaction of deposited particles with a support, chemical modification of particles, the thermal stability of catalysts, the restructuring processes of the atoms inside the nanoscale particles and cluster formation processes.

The report demonstrates the possibility of Ferromagnetic Resonance to get information inaccessible to other methods on the initial stages of formation and transformation of supported metal and oxide nanoparticles in a number of catalytic systems based on Pd, Fe, Co, Ni as well as studies of cluster formation processes in supercritical media.

POSTER PRESENTATIONS

PP-1

STUDY OF OPTICAL AND CATALYTIC PROPERTIES OF AG DESPENSED ON OXIDE SUPPORTS

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Silver catalysts are widely used in epoxidation of olefins. A new promising area for silver catalysts recently appeared is low-temperature oxidation of CO. Appropriate catalysts are different in silver loading, dispersion and supports. In the present study, two types of catalysts were studied: high-percent catalysts with low Ag dispersion for epoxidation of butadiene and finely dispersed low silver loading catalysts for oxidation of carbon oxide.

We prepared Ag catalysts under variation of a (1) composition and surface parameters of supports, (2) silver loading and precursors, (3) preparation technique and redox treatments. The samples synthesized were studied by UV-vis diffuse reflection (DR) spectroscopy, H_2-O_2 titration, TEM, and tested in gas-phase oxidation of butadiene-1,3 to 1,2-epoxi-3-butene and in low-temperature and selective oxidation of CO.

Specific activity of Ag/α-Al_2O_3 catalysts in epoxidation of butadiene-1,3 was shown to be in dependence on content of Cs promoter, its distribution on silver surface and Ag dispersion, the last one being, in turn, affected by silver precursor and preparation technique, in particular, character of thermal treatments.

On the contrary, silver precursor is not significant for catalysts of CO oxidation. It was shown that catalytic activity in oxidation of CO is appointed by a number of variables, such as nature of support, Ag loading and dispersion, red-ox treatment of the samples. High Ag dispersion and high-temperature oxidative treatment followed by reduction are necessary for developing high activity and selectivity when reacting with H_2 enriched gas mixtures.

Variation of preparation conditions enabled us to obtain finely dispersed supported silver species. UV-vis DR spectra of very low-percent samples (0.1% Ag) in this way prepared included bands at ~18200 cm-1, that corresponded to surface plasmon resonance of silver nanoparticles. This untypical position of surface plasmon resonance indicated the finely dispersed Ag nanoparticles to be easily oxidized [1].

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PP-2

CATALYTIC PARTIAL OXIDATION OF METHANE IN MICROCHANNEL REACTORS WITH CO-CURRENT AND COUNTERCURRENT REAGENT FLOWS

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The efficiency and life time of microchannel (MC) reactors for partial oxidation of methane (POM) depend largely on the design of MC plates with deposited catalyst and the mode of reagent flows in submillimeter channels [1,2]. The experiments were aimed at studying the work of two kinds of MC reactors, in which the specially designed microchannel plates permitted the generation of co-current (MCR-P) and countercurrent (MCR-Z) reagent flows. It was expected that the latter will help to decrease the thermal power density evolved on the front edge of the MC plates, which results from POM, and to prevent corrosion and destruction of the plates. The operation of the MCR-Z with the countercurrent reagent flow was compared to that of the MCR-P with the co-current reagent flow via analysis of temperature profiles and parameters of the POM, such as the methane conversion and selectivity to CO. The data on the temperature measured at the inlet and outlet of the reactors as well as on the front and back edges of the MC plates suggest that the highest difference between the temperatures of the inlet flow and the MC plate front edge is observed at highest flow rates. The temperature difference appears to be 95 and 60^0C for the MCR-P and MCR-Z, respectively. The temperature difference along the MC plate is 3.3 times higher in the MCR-P than that in the MCR-Z.

There is a good correlation between the experimental temperature differences of the front edges of plate in MCR-P and MCR-Z and the calculated heat release versus the rate of inlet reagent flows due to the POM process and almost complete conversion of the oxygen in the narrow frontal layer of the MC plates. As the MC reactors operate at convenient POM conditions both the methane conversion and selectivity to carbon monoxide differ only by few percent for the MCR-P and MCR-Z. However, after elevating the heat loads, a decrease in both characteristics is observed being much higher in the MCR-P. In addition, the front edge of the MC plates is destroyed under the action of high heat loads only in the MCR-P, which confirms advantages of countercurrent reagent flows in MC reactors.

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PP-3

SINGLE-STAGE WATER GAS SHIFT PROCESS OVER THE HEAT-CONDUCTING CATALYSTS

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Water gas shift reaction is widely used for production of the hydrogen. The industrial process of water gas shift has two adiabatic stages with the intermediate heat removal. Traditionally catalysts are used in the form of cylindrical tablets or extrudates. The efficient process has to be performed in a single-stage reactor with controlled temperature profile along the catalyst bed. Catalytic active thermal conductive composite plates (TCP) are the solution of the radial heat transfer problem in catalyst layer. TCP composition involves catalytic active component, heat-conducting reinforcing component and porophore material. Fig.1 shows the optimized form and the scheme of TCP arrangement in reactor. Fig.2 demonstrates the optimized and achieved temperature profiles for the catalysts in the form of TCP and traditional pellets.

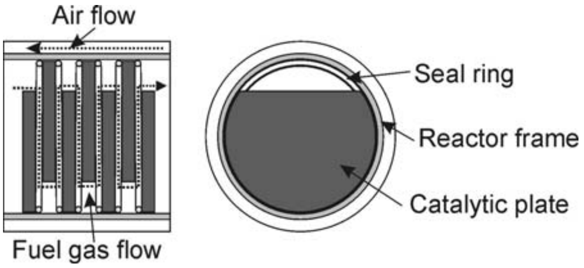

Fig.1 The scheme of thermal conductive composite plates arrangement in catalytic reactor

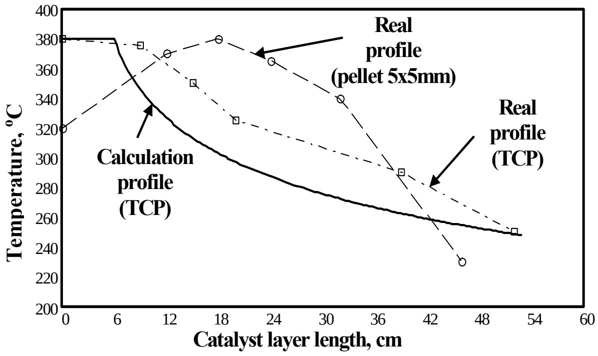

Fig.2 Experimental temperature profiles, achieved at 6000 h^{-1}, CO$_{inlet}$ 15 vol.%

Novel schemes of the heat-transfer with use of the heat-conducting composite catalytically active materials [1,2] may allow approaching the optimal temperature field in fixed catalyst bed and improving the process performance. The application of such schemes requests new high-performance catalysts, which can stably operate in a wide temperature range, e.g. those described in recent patents [3,4].

In this study we demonstrate advantage of the use the catalyst in the TCP form in contrast with catalyst of the traditional form in application for the single-stage water gas shift reactor.

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PP-4

HYDROISOMERIZATION OF BENZENE ON PLATINUM MORDENITE-ALUMINA CATALYSTS

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Process of hydroisomerization of a benzene-containing fraction (either medium straight run 70-85°C or light reformate) is available for reducing of the benzene level in a finished gasoline. In the work a series of platinum mordenite-alumina catalysts were prepared, characterized and studied in the reaction of hydroisomerization of the model feed (benzene and a binary mixture of 20 wt.% benzene and 80 wt.% n-heptane) in a down-flow fixed-bed reactor under the following conditions: P = 15 bar, T = 200-320°C, LHSV = 2 h^{-1}, hydrogen/hydrocarbons molar ratio = 3.

In the report the data of investigations of dispersion, charge and localization of the platinum on zeolite-based carrier are given. The results of investigations of samples acidity by NH_3-TPD show that the acidity decreases with decreasing the content of mordenite in the carrier. The changing of acidity occurs additively and temperature shift of the acidity maximums are not observed. Comparison between the catalytic results and acidity data show that decreasing of catalysts activity directly correlate with lowering of catalyst acidity.

The observed reaction of benzene hydroisomerization includes the stage of hydrogenation of benzene to cyclohexane (CH) and the stage of isomerization of the latter to methylcyclopentan (MCP). Straight-chain heptane partly isomerizates to branched-chain one.

The research of the effect of H-mordenite/alumina ratio on the model mixture conversion and hydroisomerization selectivity showed that the optimum mordenite percentage in the catalyst is about 20-30 wt%. At these contents, yield of MCP reach the close to equilibrium value at 280-310°C. At the work the optimal conditions for hydro-improvement of a benzene-containing fraction were determinated.

Acknowledgements

The authors thank Gulyaeva T.I. and Ponomaryova G.A. for their participation in physicochemical studies of the samples.

PP-5

DEVELOPMENT OF LABORATORY SETUP FOR OXIDATIVE METHANE CONVERSION PROCESSES

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Methane is the main component of natural gas, which reserves are comparable to those of oil. However, since natural gas is available mostly in remote areas, its transportation is inconvenient. This has led to extensive efforts to develop processes for converting methane into easier transportable, value-added products [1]. Such processes involve catalytic oxidative conversion of methane. Among them are indirect methods (conversion to synthesis gas [2] and then to methanol, ammonia or hydrocarbons) and direct methods (oxidative coupling [3], partial oxidation to methanol and formaldehyde) [4].

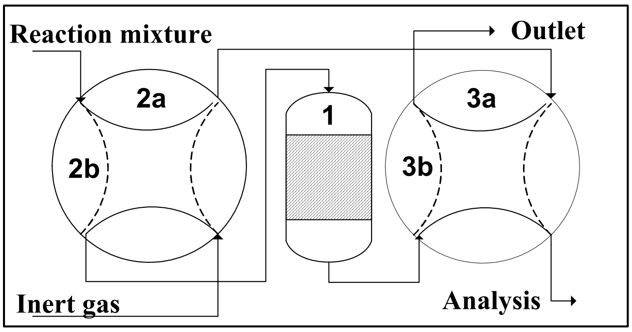

Fig 1. Experimental setup (reactor in-/outlet) for oxidative methane conversion processes.

In order to study kinetics of some representative reactions over various types of catalysts, the experimental setup was developed (Fig 1.). Setup is equipped with quartz reactor 1 in low-inertia furnace, allowing to perform catalytic experiments with precise flow (100-200 ml/min) and temperature (up to 900°C) control, in pulse and continuous regimes. Pulse regime (switch valve 2a↔2b) allows fast primary screening of catalysts, while in continuous regime (valve position 2b, 3a) conversion and selectivity of reaction and catalyst stability can be characterized. Analysis is accomplished using SRS QMS 300 Gas Analyzer. Compared with gas chromatography, mass-spectrometry has quicker response time, allowing pulse experiments and simultaneous multi-component measurements.

Thus, the kinetic setup for the studies of catalytic oxidative methane conversion has been designed and assembled. The setup allows to precisely control flow of inlet reaction mixture and reactor temperature, both in the pulse and continuous regimes. Analysis of both inlet and outlet reaction mixtures is being done rapidly by a quadrupole mass-spectrometer. At the moment, the setup is being used in the European FP7 Project.

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PP-6

SELECTIVE OXIDATION OF ALCOHOLS OVER Ag-CONTAINING SI_3N_4 CATALYSTS

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Ceramic materials based on silicon nitride provide such advantageous properties as high thermal conductivity, high hardness and strength, and therefore, can be considered as promising materials for application as a silver catalyst supports to be used in selective oxidation of alcohols into carbonyl compounds. The aim of the present work was to perform a comparative investigation of Ag-containing catalysts supported on silicon nitride during the selective oxidation of ethylene glycol and ethanol into corresponding aldehydes.

Ag-containing silicon nitride catalysts were prepared by deposition of CF_3COOAg layers on the support surface (Si_3N_4, S_3N_4-Zr and Si_3N_4-Al). In results highly stabilized Ag particles with homogeneous distribution were obtained [1]. It was shown that glyoxal selectivity was 41 % while ethylene glycol conversion was 76 % for Ag/ Si_3N_4 catalyst prepared from organic media. It was shown that the presence of ZrO_2 and $Si_3Al_{12}O_9N_{10}$ phases in the support composition allowed increasing the glyoxal selectivity up to 54 % at 97 % glycol conversion. It was shown that the support phase composition did not influence the selectivity/activity of catalysts during the ethanol oxidation in oxygen-rich reaction mixture.

Ag-containing ceramic catalysts were characterized by high selectivity/activity in the course of ethanol oxidation into acetaldehyde at 300 ^{o}C. It is noteworthy that the high values of selectivity up to 95 % and alcohol conversion 100 % mentioned were observed in oxygen-rich reaction mixture, where oxygen content was 18 %vol., ethanol content was 2 %vol. It was shown that the support phase composition did not influence the selectivity/activity of catalysts during the ethanol oxidation in oxygen-rich reaction mixture.

Mechanism of the formation of active sites on the catalyst surface during the processes of selective alcohol oxidation in to carbonyl compound was proposed.

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PP-7

THE ROLE OF PD CLUSTERS AND $Pd_XCe_{1-X}O_2$ SURFACE PHASE IN LOW-TEMPERATURE CO OXIDATION

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Catalysts based on platinum group metals supported on the rare earth oxides are among the most widely studied systems in oxidative catalysis. In particular, the catalysts of Pd/CeO_2 show high activity in CO oxidation at low temperatures T <150°C. The active sites and reaction mechanisms of low-temperature oxidation (LTO) of CO have not been studied until now. We have previously shown [1] that the active component in Pd/CeO_2catalysts, the ignition temperature of the reaction CO + O_2 which can reach 0°C or less, is presented in two forms: a palladium-oxidized interaction phase (POIP) as a substitution solid solution $Pd_xCe_{1-x}O_2$ in the surface layers of the lattice of cerium oxide and palladium reduced interaction phase (PRIP) as a palladium clusters epitaxially bound with the surface of microfacets CeO_2(111).

In this paper by a combination of XPS, FTIRS and HRTEM the Pd/CeO_2 catalysts with different support morphology controlled by the method of preparation were studied. It is shown that the catalyst based on highly defect support has on its surface palladium, mainly, in the POIP form. Then, as the deposition of palladium on low defect support leads to the appearance of palladium reduced interaction phase as small clusters of palladium. All catalysts are characterized by the same ignition temperature about 0°C determined by light-off CO. Catalyst containing clusters has a high activity in the LTO CO over the entire temperature range, whereas the activity of catalyst containing no palladium clusters, decreases when the temperature reaches 50°C and reaches a level of 100% conversion only at 150°C. Thus, the ignition temperature is determined by POIP, while palladium clusters determine the catalytic activity in the temperature range 50 - 150°C.

This work was supported by the Ministry of Education and Science of the RF (project No. 14.740.11.0419) and SB RAS Integration Project No. 112.

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PP-8

THE ROLE OF H_2O IN LOW TEMPERATURE CARBON MONOXIDE OXIDATION ON Pd/CeO_2 CATALYSTS

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The catalysts resistance to wet poisoning is the serious problem for it practical application for purification of air containing carbon monoxide. In our experiments it was shown that the Pd/CeO_2 catalyst had high activity in carbon monoxide oxidation under near-ambient temperature [1] but its stability in the presence of moisture was questionable to date. In the present work, the interaction of 1% Pd/CeO_2 catalyst with CO as well as with $CO+H_2O$, $CO+O_2$ and $CO+O_2+H_2O$ mixtures at ambient temperature was studied by catalytic testing and FTIR spectroscopy methods. The influence of humidity on Red-Ox properties of the catalyst, and reaction intermediates formation during CO oxidation was discussed.

The 1% Pd/CeO_2 catalyst demonstrated 80% CO conversion at 20°C. The addition H_2O into the gas mixture was found to decrease the activity in steady-state condition (Fig. 1). According to FTIRS data the sites including partially charged small metallic clusters in the vicinity of Pd^{2+} species were formed on Pd-catalysts under $CO+O_2$ mixture in steady-state condition. It was shown that the saturation of the support surface by more than 50% with adsorbed water blocked the reversible reaction of CO and O_2 with an active surface of Pd/CeO_2 catalyst. As a result the catalyst was extremely reduced with only Pd^o formation (Fig. 2) which apparently led to deactivation of the catalyst in the CO oxidation.

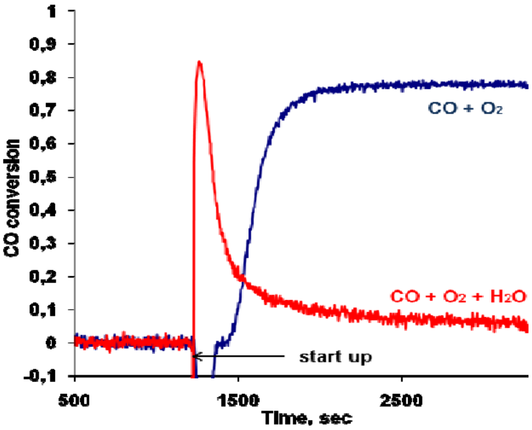

Fig. 1. Catalytic testing: 20°C, CO–0.01, O_2–5, Ne–0.5 vol.%, He balance; 200 cm^3/min

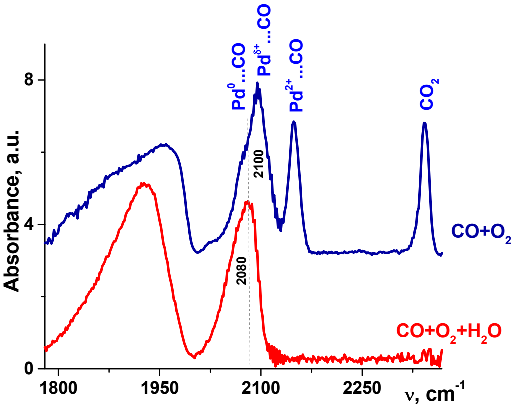

Fig. 2. FTIR data: 20°C, $CO:O_2$=1:5, time of exposure - 60 min

This work was supported by the Ministry of Education and Science of the RF.

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PP-9

FORMIC ACID DERIVED FROM BIOMASS FOR HYDROGEN PRODUCTION AND OLEFINS HYDROGENATION

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Formic acid (FA) is a by-product of acid catalysed hydrolysis of biomass [1]. Catalytic hydrogen production from FA (1) and vapour phase transfer hydrogenation of olefins by FA (2) have been studied over supported metallic catalysts (Pd, Pt, Au, Cu and Ni).

$$HCOOH \rightarrow H_2 + CO_2 \qquad (1), \qquad HCOOH + C_2H_4 \rightarrow CO_2 + C_2H_6 \qquad (2)$$

1 and 10 wt.% Pd/C catalysts were the best catalysts for the hydrogen production showing high activity, selectivity (95-97%) and stability at low temperatures (373-473 K) (Fig. 1). However, the reaction was inhibited by CO and in less extent by H_2. Ethylene could be effectively hydrogenated by FA over these catalysts to ethane (Fig. 1). Hydrogen was not found in gas phase at low conversions as it was consumed in the hydrogenation. It was shown that the hydrogen formation from FA was the rate determining step followed by the fast step of the olefin hydrogenation. A 10 wt.% Cu/MgO catalyst was cheap, stable and selective catalyst which could be used at higher temperatures (473-573 K) for the hydrogen production from FA, but not for the hydrogenation of olefins.

Thus, it is important that using of FA for the hydrogenation eliminates the need for a separate step of H_2 production. This approach may have applications in deoxygenation of some biomass derived chemicals necessary for the production of fuel additives. The catalysts were characterized mainly by TEM and BET surface area measurements.

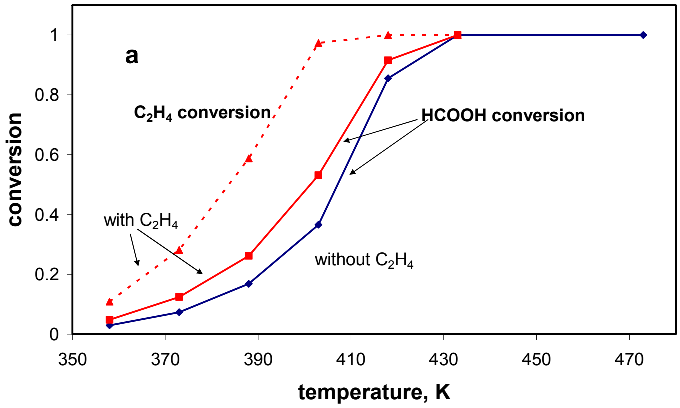

Figure 1. Conversions as a function of temperature for the decomposition of FA and hydrogenation of C_2H_4 by FA over the 10 wt.% Pd/C catalyst (6.8 mg). Total flow rate - 51 ml/min, 2.4 vol.% FA/He and 2.4 vol.% FA/1 vol.% C_2H_4/He, respectively

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FAST PYROLYSIS OIL CATALYTIC HYDROTREATMENT FOR BIOFUEL PRODUCTION: MODEL COMPOUND STUDY

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At the present time biofuels production from the lignocellulosic biomass is attracting much attention because of the depletion of petroleum deposits and the increasing environmental concern with the burning of nonrenewable resources. Fast pyrolysis being a promising biomass processing technology yields a liquid biofuel - so called bio-oil [1]. It is to be noted that the high oxygen content and chemical complexity of biomass pyrolysis oil account for its instability against heat, acidity, corrosiveness, etc. and make bio-oil unsuitable for direct use. The quality of bio-oil can be improved by the catalytic hydrotreatment or hydrodeoxygenation (HDO). HDO is performed at high temperatures and hydrogen pressures in the presence of a catalyst and consists in partial or total elimination of oxygenates presented in pyrolysis oils [2]. Extensive research of crude bio-oil and model compounds catalytic hydrotreatment has been conducted using conventional sulfided Ni(Mo), Co(Mo) hydroprocessing catalysts and supported noble metal catalysts [2,3]. But the studies undertaken showed a strong need in new catalytic systems with low cost, non-sulfided nature, high activity in the HDO process, stability against coke formation and ability for multiple regeneration. Besides due to the chemical complexity of pyrolysis oils optimization of the HDO process is needed for full refining and improvement of unwanted properties and characteristics of these oils.

In the present study a series of Ni-based catalysts supported on different materials has been tested in the hydrodeoxygenation of guaiacol positioned as a model of bio-oil. Some catalysts contained copper as a promoter, primarily to facilitate nickel reduction at temperatures lower than 300 ^{o}C. Initial screening studies on the supported NiCu catalysts showed their potential for vegetable oil hydrodeoxygenation [4]. Guaicol HDO has been carried out in an autoclave at 320 °C and a hydrogen pressure of 17 MPa. The main products were cyclohexane, 1-methylcyclohexane-1,2-diol, cyclohexanone (aromatic ring reduction products) and benzene. A guaiacol conversion scheme explaining the formation of the main products has been suggested. The highest activity was shown by the Ni-based catalysts prepared by the sol–gel method with SiO_2 in the catalyst composition acting as a structure-forming agent. According to XRD, XPS and HRTEM data, the high activity of these catalysts is due to the high nickel content and high dispersion of metal particles being formed during the reduction of nickel oxide and nickel silicate species constituting the catalyst structure. The catalysts concerned demonstrated their potential in hydrocarbon fuels production during catalytic upgrading of bio-oil. In addition, the guaiacol HDO has been carried out at 280, 320 and 360 °C under hydrogen pressure of 17 MPa. The results obtained for model compounds may be important to provide insight into the reaction pathways under different conditions in the case of crude bio-oil, and thus may be useful for the optimization of the HDO process to get upgraded products with the desirable characteristics.

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PP-11

REACTION KINETICS MEASUREMENTS AND ANALYSIS OF CATALYST DEACTIVATION FOR CONVERSION OF A-PINENE OVER Au/γ-Al_2O_3

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Terpenes, extracted from the renewable sources, such as α-pinene, are readily available and contain functional groups, providing renewable starting materials for the production of a wide variety of valuable fine chemicals. Camphene, a precursor of camphor which is an important substrate for the pharmaceutical and perfumery industry, is commercially produced by α-pinene isomerization in the liquid phase over acid-hydrated TiO_2 resulting in camphene yield from 35% to 50% [1]. The Au/γ-Al_2O_3 catalyst was demonstrated recently to be rather active in the vapour-phase α-pinene isomerization to camphene with conversion 99% and very high selectivity of about 60-80% [2].The objective of this work is to study the peculiarities of α-pinene conversion to camphene over Au/γ-Al_2O_3 catalyst.

The isomerization of α-pinene to camphene was carried out in vapour-phase by using a fixed bed glass reactor within temperature range 463÷483 K at atmospheric pressure using *n*-octane as a diluent. The effects of temperature, residence time and initial α-pinene concentration on the α-pinene conversion and the camphene selectivity were studied. Experimental data showed that the reaction rate was close to first-order in α-pinene. The main products are formed in parallel ways and their selectivity did not depend on the reaction temperature. The values of the main kinetic parameters in α-pinene isomerization over Au/γ-Al_2O_3 catalyst were determined. The detailed investigation of catalyst deactivation during α-pinene isomerization was also performed. According to TPO and UV-Vis-mass *in situ*, as well as TEM it was found that catalyst deactivation in the course of reaction is caused by deposition on the gold particles the $C_{10}H_{16}$ compounds. The initial catalyst activity was shown to be regenerated completely by the oxygen thermal treatment.

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

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PP-12

CATALYTICALLY ACTIVE MEMBRANES BASED ON COPPER AND CERIUM OXIDES: EFFECT OF DOPING

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The problem of air pollution abatement from exhaust gases is substantially related to the oxidation of carbon monoxide. Current development on combustion catalyst is focused on improving of the catalytic activity, including the search of better support materials for the active component to provide effective gas diffusion to active centers with low-pressure drop in the reactor and to solve the problem of surface contamination. A combining the membrane system with catalyst could be used to solve this problem [1].

This work is devoted to adapting of the surface self-propagating high-temperature synthesis (SHS) for supporting the catalytic active layers based on copper and cerium oxides over the surface of membranes. The catalytic performance of CuO-CeO_2 system doped with various metal oxides (Fe, Co, Ni and Mn) was studied. The morphology and phase composition of prepared catalysts were characterized by XRD, elemental analysis and SEM.

The fiberglass tissue was chosen as a model support for deposition of catalytically active layer. This kind of substrate is characterized by high heat resistance (up to 1200 °C). The samples prepared by SHS have been investigated in the model reaction of CO oxidation. The correlations between catalytic activity and chemical composition of the samples were found. The structure and morphology of the active oxide layers have also been studied. The developed technique of supporting of the doped copper-cerium layers was ultimately used for the preparation of the catalytically active membranes.

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PP-13

Co-PROCESSING BENZENE FRACTION OF GASOLINE OBTAINED BY CATALYTIC REFORMING AND C_3 FRACTION OF REFINERY GAS

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The benzene fraction (NC - 85 °C) of catalytic reforming, is a major source of benzene in the gasoline pool, but by the standards of Euro-4 benzene content in gasoline should not exceed 1% by volume.

The ultimate solution to an enterprise is the allocation of benzene fraction of the feedstock reforming units with its subsequent processing, or optimization of reforming technology with the selection of a new catalyst with the reconstruction of the installation. If the first option does not lead to drastic changes in the technological scheme of the plant, then the option with the reconstruction of the unit itself will need to reassess of the hydrogen balance refineries due to rising of consumption of hydrogen.

One of the promising options to reduce the benzene content in commercial gasoline is an option of processing includes the standard scheme of reforming of a wide gasoline fraction NC-180 °C, with separation of benzene fraction of the reformers, and by subsequent alkylation of isolated benzene fraction by light alkanes (C_2-C_3) of refinery gas on hybrid catalysts.

Laboratory specimens of catalyst were prepared by mechanical synthesis of the industry catalysts platinum-rhenium imported (Axens, UOP LLC) and polycation-decationated ultrastable zeolite Y.

Catalysate contained in its structure alkylaromatic mainly isopropylbenzene (di- tert-isopropylbenzene no more than 3% wt.) and hydrocarbons i-C_{5+}. The gaseous products were represented by hydrogen, butane, propylene and unreacted propane.

PP-14

IMPROVEMENT OF ENZYME HYDROLISYS OF CELLULOSE BY MECHANICAL TREATMENT OF REAGENTS

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Biofuels and chemicals may be produced from the renewable sources. To make different products from plant raw materials may be used sustainable enzyme technology. Commercial application of enzyme hydrolysis of carbohydrates is restrained by high cost of enzymes and slow reaction rate. To improve enzyme hydrolysis of cellulose substrate different methods are usually implicated, e. g. preliminary chemical treatment of lignocellulose plant materials, its steam treatment and also mechanical treatment of reagents. In comparing with other methods mechanical treatment is sustainable technology as acids, alkali and toxic organic solvents aren't used.

On the other hand simultaneous mechanical treatment of enzyme and cellulose substrate in time of reaction may be the reason of decrease in the reaction rate, as exposed enzyme may denaturate. So study of influence of mechanical treatment of reagent on catalytic activity of enzyme is important.

In this work influence of mechanical treatment of reagents on catalytic activity of cellulase enzyme was studied. Cellulase enzyme system Cellolux - A was used (Sibbiopharm, Russia).

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[1] Winner of contest of Youth scientific projects in the field of energetic "Energy of Youth", 2010.

PP-15

SYNTHESIS OF AROMATIC NITROCOMPOUNDS BY VAPOR-PHASE NITRATION OVER NATURAL ZEOLITES

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Synthesis of aromatic nitrocompounds is an important industrial process. However utilization of nitrating mixture (HNO_3+H_2SO_4) used in large-scale industrial production of nitrobenzene (NB) becomes a serious ecologic problem [1]. The gas-phase benzene nitration is known to be an alternative to this process [2]. Here we report preliminary results on the benzene nitration catalyst development.

Natural zeolites can be used as solid acid catalysts for some fine or bulk chemistry processes [3]. The samples of the pretreated (fractionation 0.25-0.5 mm) and calcined (450°C) natural zeolites have been tested as vapor phase nitration catalysts. H-ZSM-5 zeolite was used as a reference sample. Catalytic experiments and the reaction mixture analysis were performed according to the reported procedure [4].

The catalytic performance of non-modified natural zeolites derived from the Far-East region (Russia) was studied. In subsequent experiments we studied the activity of dealuminated samples of the natural zeolites. We found the correlation between the samples acidity (studied by CO-sorption IRS), as well as the content of the crystalline forms in the zeolite and theirs catalytic activity.

The results obtained allow one to consider the natural zeolites as promising catalysts for heterogeneous gas-phase benzene nitration.

The work was financially supported by Siberian Branch of Russian Academy of Science (Integration project No. 144).

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PP-16

INVESTIGATION OF MICROALGAE CATALYTIC PROCESSING

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World energy consumption is supposed to increase over the next few decades as well as transport fuel demands. Renewable biofuels are needed to partially displace petroleum derived transport fuels. Liquid biofuels might help to avoid lack of transport fuels, to decrease fuel prices in future and more over to reduce green house gas emissions. Currently, different types of biofuels (e. g. biodiesel, bioethanol, biobutanol etc.) are derived from different types of biomass. Biodiesel is mainly associated with mono-alkyl esters of long chain fatty acids produced by transesterification process from vegetable oil, animal fats and waste cooking oil. Although, agricultural crops are used for biodiesel production, they have some disadvantages. For example, fuel production from edible crops influence on food prices and agricultural crops do not have enough oil productivity for commercially successful fuel production. Microalgae are believed not to influence on food prices in comparison with edible agricultural crops and most productive oil crops, such as palm oil do not come close to microalgae in their ability to produce so much quantity oil per area [Y. Chisti, 2008]. Nowadays homogeneous catalysts (e. g. NaOH, H_2SO_4 etc.) are used in transesterification process. The final mixture needs to be separated, neutralized and thoroughly washed, generating a great amount of salt, soaps, and waste water which need to be further purified and treated. It is to be mentioned that the catalyst cannot also be recycled [R. Luque, 2008]. Biodiesel has a number of restrictions due to its higher viscosity and cloud point in comparison with conventional diesel. Therefore oxygen removal by different processes (e. g. hydrodeoxygenation or pyrolysis) is required for production of hydrocarbons suitable for diesel fuel blending [D. Yu. Murzin, 2005].

The aim of our study was the investigation of different catalytic processes for biofuel production using microalgae as a feedstock. The esters (biodiesel) were derived by transeresterification process from lipid fraction of microalgae *Botryococcus braunii* UTEX 2441. The process was conducted over homogenous catalyst (H_2SO_4) and heterogeneous catalyst ($BaAl_{12}O_{19}$) the experiments were carried out in batch reactor. The hydrocracking process was applied for oxygen-containing groups removing (ester functional group in this case). This process was conducted over Ni - based catalysts, having been reported as good catalysts for upgrading biodiesel from rapeseed oil into conventional fuel [V. A. Yakovlev, 2009]. The experiments were performed in a conventional flow reactor with ethyl ester of octanoic acid and methyl ester of hexadecanoic acid used as model compounds. The choice of model compounds was based on experimental data and data available in literature. The maximal conversion of esters has been observed over Ni – Cu/Al_2O_3 catalyst. The hydrockracking of microalgae's lipid fraction (*Botryococcus braunii* UTEX 2441) over Ni – based catalysts has been carried out as well to derive transport fuel compounds in one step process without transesterification reaction.

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PP-17

CO ELECTROOXIDATION ON NANOSTRUCTURED PLATINUM PARTICLES WITH SELECTIVELY BLOCKED SITES

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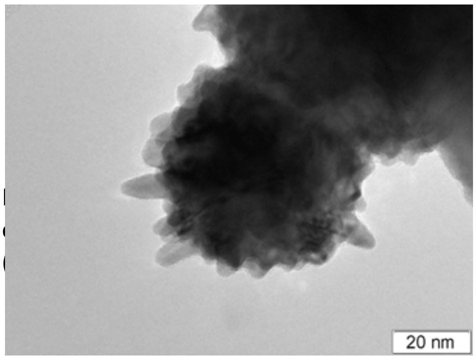
Surface defects play important role in heterogeneous catalysis. It is widely accepted that surface defects may act as active sites in various catalytic processes. Numerous studies which are related to the investigations of single-crystal metal surfaces in different chemical and/or electrochemical processes show that the presence of small fractions of defects leads to their significant acceleration. This is related to the fact that formation and reaction of active intermediates on surface defects is energy-wise advantageous. However, the nature of active sites on nanomaterials in heterogeneous catalysis and electrocatalysis is not fully understood yet. Development of new approaches and creation of suitable model catalytic systems helps in the understanding of nanosized catalysts operation, especially such phenomena like size effects and high activity of intercrystalline boundaries.



As a model electrocatalyst we have chosen nanostructured platinum particles electrodeposited on a gold film. Gold film chemically deposited on a silicon substrate is a good support to study metal particles by electrochemical and in situ Infrared spectroscopic methods. The figure shows “hedgehog”-like structure composed of needle-shape Pt nanoparticles (NPs) grown on the gold substrate by electrodeposition and imaged by TEM. These platinum nanostructured particles are an attractive model system to investigate the role of surface defects. We applied selective site blocking method reported previously in [1] in combination with spectroscopic (ATR-SEIRAS) and electrochemical (cyclic voltammetry, chronoamperometry) methods to study the role of surface defects in the model CO electrooxidation reaction. We used gold as selective blocking element (SBE). The influence of gold adatoms on the CO electrooxidation reaction on electrodeposited Pt structures has been studied to confirm the possibility of an application of the chosen method and Au as a SBE. Using CO is as a surface sensitive probe-molecule and applying CO dosing procedure bare and gold-modified electrodeposited Pt NPs have been investigated by ATR-SEIRAS. The transients of adsorbed CO oxidation on gold modified electrodeposited Pt nanoparticles have also been analysed.

The work is financially supported by ANR under the project ANR-06-CEXC-004 and by the scholarship of the Boreskov Institute of Catalysis.

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PP-18

SOLVENTS INFLUENCE ON THE STRUCTURE OF TUNGSTEN PEROXO COMPLEX $[CH_3(N\text{-}C_8H_{17})_3N]_2\{HPO_4[WO(O_2)_2]_2\}$ AS A CATALYST FOR SELECTIVE OLEFIN EPOXIDATION

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The tungsten containing peroxo species (which formed in the system of H_2O_2-$H_3PW_{12}O_{40}$) are used widely in the green chemistry as catalysts for selective olefins oxidation process. Usually X-ray diffraction is used for study of structure similar compounds in the solid state. Nevertheless such catalytic reaction going into the solution and we have not enough information about these complexes structure which dissolved in organic solvents. It has been found that activity and selectivity these catalytic reaction depends on type of organic solvents [1]. The possible hypothesis of these phenomena is influence of solvent on the complex structure or aggregation several complex units into the one large oligomer particle. Also some steric effects can influence on activity and selectivity such complexes.

So, the aim of our work is identify of solvents influence on the structure of $[CH_3(n\text{-}C_8H_{17})_3N]_2\{HPO_4[WO(O_2)_2]_2\}$. This compound has good catalytic properties in the reaction of olefin selective epoxidation. The small angle X-ray scattering (SAXS) technique it should be used for understanding structure of this compound in different series polar and non-polar solvents. It has been found than more polar properties of solvent than less R_g (radii of gyration) which correlate with a real size of tungsten containing complex. Depending of the solvent nature R_g value is changing more then 3 times. This fact is supported hypothesis about aggregation of tungsten containing peroxo species in the some solvents. So, it can be used for explanation experimental data about different activity and selectivity tungsten containing peroxo species in the different solvents.

The work was supported by the Branch of General and Technical Chemistry RAS (Project 5.7.3.).

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PP-19

TOWARDS THE EFFICIENT GREEN OXIDATION OF ALCOHOLS

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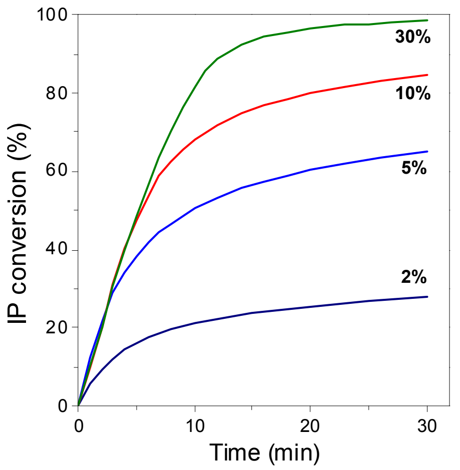
The catalytic oxidation of alcohols with oxygen as the oxidant and water as solvent – ideal conditions for economy, environment and safety – is a challenging task in fine organic synthesis, energy technologies, environmental science, and other important fields. The catalyst productivities are still below 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 present evidence that excellent catalytic performance is possible even with the low-reactive substrates, while retaining the reaction conditions still 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 in the catalyst) 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). Experiments with promoted catalysts and other alcohols are to be performed.



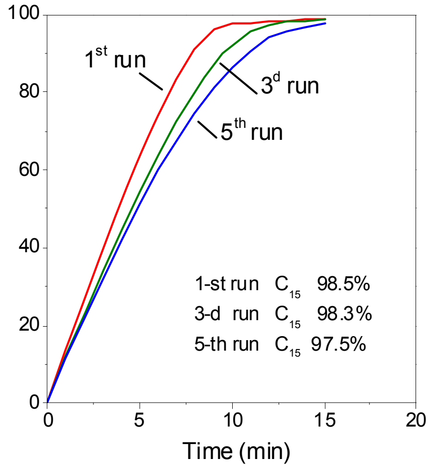


Fig. 1 (left). Catalytic performance of Pt/C samples prepared through hydrolytic deposition and differed in Pt loading (wt% is shown near the curves). Conditions: H_2O 9.5 ml, IP 6.5 mmol, O_2 1 bar, 30 °C. Catalyst mass 5-75mg but the mass of Pt in the reactor constant (7.5 μmol).

Fig. 2 (right). 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).

PP-20

NANOSIZE COBALT BORIDE FORMATION IN REACTION MEDIUM OF BORON-BASED COMPLEX HYDRIDES

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Over the past 10 years, metal borides have been intensively studied due to their unique electronic, magnetic and catalytic properties. Special attention is given to cobalt borides as low-cost and efficiency catalysts for the hydrolysis of complex hydrides ($NaBH_4$, NH_3BH_3). This process is important for generation of high-purity hydrogen for portable power systems [1]. A traditional way of cobalt borides preparation is the direct combination of powdered Co and B at temperatures above 1000°C. However, cobalt borides are also formed in the reduction of cobalt salt solutions with $NaBH_4$ or KBH_4 at ambient conditions. It is to be noted that in this case, amorphous nanosized cobalt borides are formed [2].

In this work we have studied the formation of cobalt boride depending on the nature of the reducing agent ($NaBH_4$, NH_3BH_3), and the initial cobalt compound ($CoCl_2$, Co_3O_4), as well as their activity in the hydrolysis of $NaBH_4$ and NH_3BH_3. Samples have been characterized by magnetic susceptibility method, FTIR, XRD, TEM. It was shown that Co compounds were reduced under the action of $NaBH_4$ solution with a formation of amorphous ferromagnetic catalytic active phase of cobalt boride with Co_2B composition and average particle size around 30 nm. Catalytic activity of initial Co compounds is directly related to their reduction rate and content of active ferromagnetic cobalt boride phase formed in reaction medium. The reduction of Co compounds in the NH_3BH_3 solution proceeds at a slower rate than in the $NaBH_4$ solution. The addition to the solution of NH_3BH_3 of even a small amount of $NaBH_4$ increases the reduction rate of $CoCl_2$ and Co_3O_4 considerably. In conclusion, initial Co compounds and hydride medium are the determinative factors influencing the physicochemical and catalytic properties of cobalt borides. On the basis of the catalyst activity and stability data, the nanosize cobalt boride formed *in situ* from Co_3O_4 under the action of aqueous $NaBH_4$ is a promising catalyst for hydrolysis of $NaBH_4$ and NH_3BH_3 [3].

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PP-21

KINETIC MODELLING OF CATALYZED OXIDATION OF SOOT

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Car population grows from year to year, including vehicles with diesel engines. Diesel engines have some advantages against gasoline ones, but a large amount of carbon particles are emitted in the atmosphere with diesel exhaust. Fine soot particles inhaled by humans do serious damage to their health resulting in such dangerous disease as cancer of lung.

Wall-flow monolith filters are commonly used for soot abatement in diesel exhausts. Soot particles are separated from the gas phase by filtration and accumulated in channel wall pores dramatically increasing the pressure drop through a monolith. So the burning of soot particles inside the filter is needed. Soot burns at approximately 550-600^{0}C with oxygen, while diesel exhaust gases temperature lies between 200 and 400^{0}C. To force soot burning at these temperatures catalyzed oxidation is preferably used. The great number of studies reported in literature concerns soot oxidation catalysts. The comparison of the catalyst performance is usually based on the light-off temperature, but this parameter may depend on experimental conditions. The better parameter for comparison is the activation energy for the process. Furthermore, the activation energy data are needed for the modeling and design of the catalyst soot filters [1].

The paper is devoted to kinetic modeling of soot oxidation over $CeO_2/\theta\text{-}Al_2O_3$, $Pt\text{-}CeO_2/\theta\text{-}Al_2O_3$ and $Fe\text{-}Mn\text{-}K\text{-}O/\gamma\text{-}Al_2O_3$ catalysts with gas mixture containing oxygen, nitrogen oxide, sulfur dioxide and water. Temperature programmed oxidation experiments were performed in a home built reactor described elsewhere [2]. The following equation has been used to derive the activation energy E_a and the Arrhenius pre-exponential factor k_0 [3]:

$$-\frac{dm}{dt} = k_0 \cdot e^{-E_a/RT} \cdot y_{O_2}^{\alpha} \cdot m_0 \cdot \left(m/m_0\right)^{\beta},$$

y_{O_2} is the partial pressure of oxygen; m_0 and m are the initial and instantaneous soot mass in the reactor, respectively; R is the molar gas constant; T is the absolute temperature; t is time. Fixing partial order of oxygen (α) and one of soot (β) the kinetic parameters were estimated using EVM (Errors in Variables Model) method with numerical integration.

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PP-22

OLIGOMERIZATION OF OLEFINS REFINERY GASES IN CATALYTIC SYSTEMS «HPA/MCM-41»

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Deepening of refining requires the development of secondary refining processes (catalytic cracking, thermodestruction processes of heavy oil residue processing, etc.) that are accompanied by significant release of gaseous by-products, on average 5-8% wt. from the amount of refined oil to refineries.

One of the areas of rational use of refinery gas is the process of the catalytic oligomerization of olefins, which allows receiving valuable components of such as gasoline and diesel fuel.

Authors for the oligomerization of olefins by refinery gases proposed catalytic systems - heteropolyacid 12 series of structure Keggina - $Ni_{6-x/2}H_x[SiW_{11}NiO_{39}]\cdot 23H_2O$ heterogenized on mesostructured silicated material MCM-41. HPA was introduced by impregnation, dried at a temperature of 110-150 °C and calcined at 350 °C. Olefin oligomerization process C_3-C_4 was performed in a flow-circulation reactor at 150 °C, pressure 4.0 MPa and flow rate of raw material feeding 1 h^{-1}. Conversion of olefins was 70-74% wt., selectivity for isoolefin 85-87% wt.

PP-23

FAU STRUCTURE ZEOLITES AND IONIC LIQUIDS - MODERN TRENDS IN THE DEVELOPMENT OF ALKYLATION PROCESS

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In the strategic development priorities of the Russian refining major focus is to create technology for the alkylation of isobutane by olefins on solid-acid catalysts.

Alkylation of isobutane by olefins, practically the only process which allows high-quality component of gasoline, the percentage of involvement which in the fuel is limited only by existing production resources. Analysis of the process development of solid-acid alkylation showed that the establishment of effective heterogeneous catalysts lies in the use of zeolites, mainly faujasite type (structure type FAU) [1].

So, in collaborative research to develop zeolite catalyst alkylation catalyst held Faculty «Technology of Oil and Gas» Ufa State Petroleum Technical University, «CATACHEM Company» and the Division of Fuel «Institute of Petroleum Refining and Petrochemistry of the Republic of Bashkortostan» have been developed and investigated catalytic systems based on zeolite type Y. No matter how the researchers had hoped to create a process for alkylation on heterogeneous catalysts, it is impossible not to note their shortcomings - not long lifetime (no more than 40-50 hours) and the creation of a high ratio of isobutane/olefin for the effective conduct of the process.

In this regard, the authors were continued the search for alternative options for the holding of alkylation process. One such option is the use of ionic liquids (IL) as a catalytic medium, which allows combining the properties of liquid acids and are environmentally safe. The conducted investigations in this direction have already showed some effectiveness: the ability of simplicity to regenerate itself IL, high performance (due to the low ratio of isobutane/olefin) and, most importantly the possibility to reconstruct the existing facilities.

Thus, we conclude that further development of the alkylation process can be characterized by two trends: the continuation of development in the optimization of zeolite catalysts (based on zeolite type Y) and the development of process using ionic liquids.

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PP-24

MEMBRANE REACTORS FOR HYDROGENATION REACTIONS

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The efficiency of using the permeable composite material (PCM) is demonstrated in three types of catalytic reactions: (1) in the 3-phase reaction of two gaseous reactants giving liquid products (PCM acts as a contactor catalytically active membrane) - Fischer-Tropsch synthesis; (2) in the 2-phase reaction controlled by internal diffusion and heat transfer (PCM acts as a structured catalyst bed) - preferable CO methanation in CO_2 containing gas; (3) in the 3-phase reaction of liquid substrate hydrogenation (PCM acts as a catalytically active contactor) - hydrogenation of fatty acid triglycerides. Permeable catalytic material contains oxide catalysts of different compositions and structures. Under reduction conditions metal nano-particles are formed for all studied catalysts. There for PCM performs a structured catalytic layer contained nanoscale metal particles.

Fischer-Tropsch synthesis. PCM membrane reactors allow performing the Fischer-Trospch synthesis with high productivity of the reactor: upto 50-70 kg $(m^3\ h)^{-1}$ at 1 bar, upto 120 kg $(m^3\ h)^{-1}$ at 11 bar and with high selectivity ($\alpha \geq 0.85$; C_{5+} 0,7-0,9). The advantages over existing processes are: absence of the problem of wax/catalyst separation (the catalyst is fixed in the membrane), no need in the huge height required by the traditional slurry reactors (horizontal arrangement is preferable for PCM).

Preferable CO methanation in CO_2 containing gas. The permeable composite material (PCM) based on NiCr oxide catalyst provides the fine fuel gas purification by CO preferential hydrogenation down to residual CO concentration of 6–20 ppm and below and ensures the high selectivity above 0.5 in the wide range of GHSV from 6000 to 17,000 h^{-1}.

Hydrogenation of fatty acid triglycerides. Triglycerides of oleic and stearic acids are reacting with hydrogen over Cu-containing catalyst in the PCM contactors. A mixture of C_{18}-alkanes, alkenes, alcohols and acids as well as some C_{18}-C_3 and C_{18}-C_{18} esters are formed during the reaction. After cooling, the hydrocarbon mixture in reactor is enriched in high-boiling products. Volatile products of hydrogenation evaporate and condense downstream.

Permeable composite monolith (PCM) approach allows intensifying the mass- and heat transfer within the catalyst bed, which helps in significant improving productivity and selectivity of the catalytic process.

PP-25

SYNTHESIS OF GREEN DIESEL THROUGH DEOXYGENATION AND KETONIZATION OF CARBOXYLIC ACIDS

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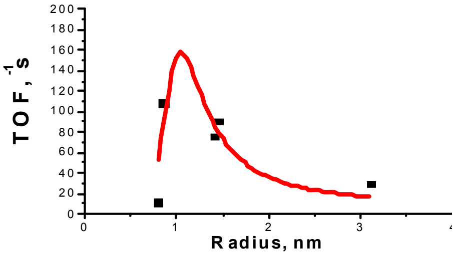
To produce green diesel fuel from renewable organic materials such as C_{16}-C_{18} acids present in vegetable oils and C_5-C_9 carboxylic acids produced for example in aqueous phase reforming of sugars and sugar alcohols, catalytic deoxygenation [1] and ketonization [2] have been applied respectively. Conversion of C_{16}-C_{18} acids into one carbon less hydrocarbons has been studied over the most promising Pd/C catalyst in lean hydrogen atmosphere with controllable Pd dispersion. Methods of TPR H_2, TPD CO, TEM, N_2 adsorption and CO chemisorption were applied to elucidate correlation between deoxygenation activity and Pd structure properties. An optimum metal dispersion and presence of species with proper metal-support interactions giving the highest catalytic activity were established (Table 1) [3]. Experimental TOF dependence *vs.* Pd size correlated well with the theory [4] (Fig. 1). Impact of mass transfer and reaction temperature was elucidated.

Table 1. Pd species distribution according to TPR H_2 for catalysts with different dispersions. Experimental TOF in C18 acids deoxygenation (300°C, 17.5 bar 5%H_2/Ar)

Pd dispersion	Pd big particles, %	Pd-O-C (I), %	Pd-O-C (II), %	TOF (s^{-1})
A (18%)	57	36	7	30
C (65%)	20	60	20	109
D (72%)	6	27	67	12

Figure 1. Effect of Pd dispersion on TOF



Vapour phase ketonization of C_5 acid (as a model compound) was studied over metal oxides ZrO_2, CeO_2, MgO, CeO_2/ZrO_2, MnO_2/ZrO_2 at T= 573÷673 K under P_{H_2}=1 bar. The effect of temperature, residence time and C_5 acid initial concentration on the conversion and selectivity to the desired ketone was investigated. Selectivity to 5-nonanone of 94% at complete conversion of valeric acid was observed over the most active ZrO_2 at 628 K.

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PP-26

PECULIARITIES OF CARBON NANOSTRUCTURES FORMATION FROM DIFFERENT CARBON-CONTAINING PRECURSORS

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Carbon nanofibers (CNF) attract great interest for potential use as a modifying agent in composite materials, in creation a conductive paints, filters and novel sorbents. The catalytic decomposition of hydrocarbons (chemical vapor deposition, CVD) becomes today the most popular way of CNF obtaining. Depending on type of hydrocarbons and composition of catalyst CNFs can be formed with different structure which is determined by the order of graphene layers packing. For CNF production it is possible to use not only pure hydrocarbons, but also their mixtures and halogenated derivatives, too. This process is therefore interesting from the point of view of solving the problem related to associated petroleum gas utilization and neutralization of toxic organochlorine wastes.

We have studied regularities of CNFs formation by the decomposition of natural gas, propane-butane mixture, and series of halogenated hydrocarbons over nickel and nickel-copper catalysts. The experiments were carried out in a quartz lab reactor and scaled-up in pilot installation equipped with rotary reactor. Morphology of the resulted CNFs material has been investigated by high resolution transmission electron microscopy. Such approach made it possible to determine the specified conditions for obtaining 3 types of CNF: coaxially-conical, platelet and feather-like ones. Last morphology of CNF is characterized by a very defective structure and high surface area which is 3-4 times higher as compared with above mentioned types of CNF. Formation of coaxially-conical and platelet CNFs were observed only in case of decomposition of hydrocarbons, while the feather-like morphology can be obtained by decomposition of both propane-butane mixture and halogenated hydrocarbons.

According to scanning electron microscopy synthesized CNFs differ not only in packing of the graphene layers, but also in secondary structure. It was found that carbon material could be represented as coiled bunches, microsprings, parallel straight carbon fibers and bimodal structures.

This work was financially supported by the Ministry of Education and Science of Russia and by the grant of the President of Russian Federation (project №MK-3711.2011.3).

PP-27

PEROSKITE-LIKE CATALYSTS FOR THE CATALYTIC WET PEROXIDE AND WET AIR OXIDATION OF PHENOL

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The processes of catalytic oxidative destruction of organic toxic substances by hydrogen peroxide and air oxygen usually use worldwide for wastewater treatment [1,2]. As catalysts for oxidation of organic pollutants often use oxides and mixed oxides of transition metals (Fe, Cu, Mn, Co, Ni), however they show low stability in aggressive media. $LaMeO_3$ perovskite-like oxides are among the promising catalysts for the oxidation owing to their high catalytic activity in oxidative reactions and high stability in aggressive media [1]. In this work we studied the activity and stability of perovskite-like catalysts in the oxidation of phenol which is a typical pollutant of wastewaters.

Perovskite-like $LaMeO_3$ (Me = Fe, Cu, Mn, Ni) oxides were prepared, characterized with XRD and N_2 adsorption and tested in oxidation of phenol by hydrogen peroxide (30°C, 1 bar) and air (130-160°C, 50 bar).

A noticeable catalytic activity was only found for $LaCuO_3$ and $LaFeO_3$ as for wet peroxide as for wet air oxidation. Oxides containing Mn, Ni, Co appeared to be inactive. Both the rate of phenol oxidation and the level of the TOC removal were much higher in case of $LaCuO_3$. XRD studies of the samples used demonstrated stability of the perovskite-like structure during the reaction. The leaching test proved heterogeneous nature of the catalyst action. Experiments with several catalytic cycles revealed the acceptable stability of the $LaFeO_3$ and catalyst.

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PP-28

REMOVAL AND RECOVERY OF METAL CATALYSTS VIA INTERACTION WITH CO

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The processing of hydrocarbons and wastes on their base are being now in area of significant interest all over the world. In our work the attention was paid to method of recycling the accompanied oil gas and chlorine-bearing hydrocarbons with production of carbon nanofibers (CNF). Nowadays CNF material has been intensively studied for creation of new reinforcing technologies of ceramics, polymers and building materials (concrete and bitumen).

CNF can be obtained by decomposition of hydrocarbons (or their derivatives) according to the mechanism of carbide cycle taking place over Fe, Co and Ni supported catalysts. After being synthesized, CNF product contains initial support and dispersed metal particles remained. The clearing of large amounts of carbon material from catalyst is known to be a real challenge.

Both chemical (etching in acids, [1]) and thermal (glowing at 1000-1700°C in inert atmosphere, [2]) methods are practically applied for purification of CNF. Mentioned methods have a number of ecologic and technological disadvantages. For example, use of a thermal way can lead to partial destruction of carbon fibers whereas etching procedure requires the additional stages to be involved in the entire process (washing, drying, and recycling of a waste).

A new way to purify CNF (carbonyl method) is offered in our work. It is based on interaction of dispersed metal particles with CO. Nickel carbonyl is known to be easily formed at relatively mild conditions. Due to its high volatility, purification can be performed without discharging the reactor from as-prepared CNF material. The released vapors of carbonyl are supposed to be adsorbed and decomposed on various substrates to give the recovered catalyst.

Series of CNF samples were produced using Ni-catalysts and various HC-precursors, including chlorine-containing. The residual concentration of metal in samples varied in the range of 3-30 wt.%. Textural properties of carbon fibers and dispersion of metal particles were characterized. The offered carbonyl method was tested for purification of CNF from the catalyst; the obtained results have been compared with traditional methods.

Research was supported by Ministry of Education and Science of Russia and by the grant of the President of Russian Federation (project № MK-3711.2011.3).

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PP-29

APPLICATION SAXS TECHNIQUE FOR STUDY DISPERSITY OF NANOPARTICLES IN THE HETEROGENEOUS CATALYSTS FOR OXIDATION PROCESSES

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As well known dispersity and structure of supported metal nanoparticles and also interaction between supported nanoparticles and supports has very important meaning by design of functional materials and catalysts.

The aim of this work is development a new procedure for getting information about structure and dispersity of metal nanoparticles which used as an active component of the heterogeneous catalysts. For solving this goal we used method of small angle X-ray scattering (SAXS) with different contrast agents. Variation of the contract level is allowed to extract scattering intensity of supported metal from general intensity of scattering. Efficiency of our approach it was shown for several samples industry catalysts. For verification our data we compared SAXS and TEM data. It was found a good agreement of both techniques. In our work we can get distribution of supported particles sizes and some evaluation degree of metal-support interaction.

In generally our approach can be useful for investigation any changing in the supports structure after catalyst preparation procedure. This technique has been tested on the different catalytic system such as (Pt, Pd, Co)/Al_2O_3, (Ni, Fe, Co)/TiO_2. So, it has been proposed a new technique for study supported metal catalyst.

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PP-30

NUMERICAL SIMULATION OF THE HEAT SHIELD IN A SHORT CONTACT TIME REACTOR

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The oxidation processes carried out on structured catalysts (e.g. gauzes and monoliths) at the short contact time ($\leq$0.1 s) are autothermal and nearly adiabatic because both gases and catalyst are heated from a low inlet temperature to typical operating temperatures of about 1000 - 1500 K due to heat release by an exothermic reaction. An inert monolith being placed in front of the catalyst serves as radiation heat shield and to promote mixing of feed. However, some operating conditions cause the temperature in the heat shield to rise conversably above that which may initiate homogeneous reactions (Fig.1).

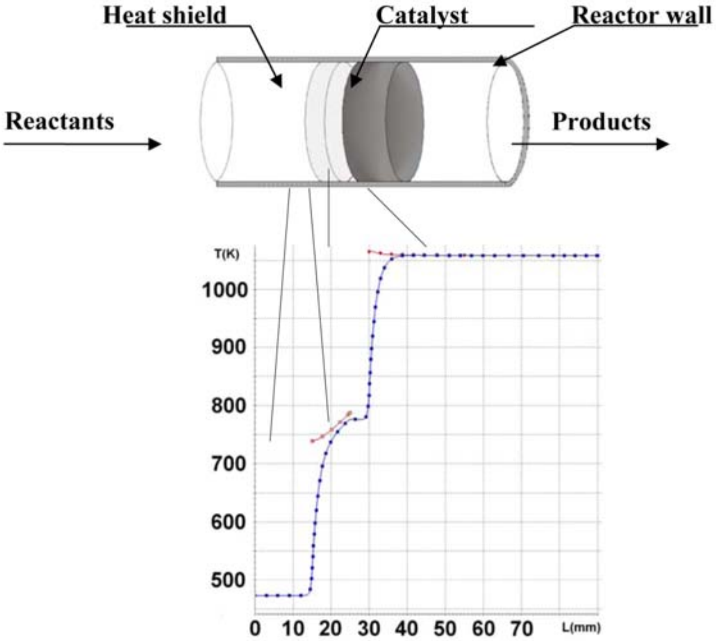

Fig. 1. Sketch of a monolith reactor and calculated steady-state surface (red) and gas (blue) temperature profiles for isooctane partial oxidation.

The objective of this investigation is a better understanding of the phenomena affecting the temperature distribution at the inlet reaction section by using numerical simulations.

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PP-31

PROCESS OF COMBINED OXIDATION OF CO AND SO$_2$ IN WASTE GASES OF NON-FERROUS SMELTERS AT PLATINUM GLASS-FIBER CATALYST

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SO$_2$ abatement in waste gases of non-ferrous smelters is an important environmental protection problem. The most effective technology for solution of this problem is the catalytic SO$_2$ oxidation reverse-process [1], but its efficiency decreases under presence of CO in gases, due to catalyst beds overheating due to exothermic CO oxidation resulting in corresponding decrease in equilibrium SO$_2$ conversion. Therefore, the development of the effective CO oxidation catalyst, capable to work stably in SO$_2$ environment, is actual. The problem may be resolved by application of the platinum catalyst on the glass-fiber support [2], which may effectively oxidize both CO [3] and SO$_2$ [4], demonstrating high operation stability in the conditions of real sulfuric acid manufactures [5].

Experiments were carried out with 0.02% Pt catalyst on Zr-Si glass-fiber support, with a mixture modeling the composition of the metallurgical waste gases. To model the long-term SO$_2$ deactivation influence we used the catalyst preliminary treated for more than 1000 hours in real gases of industrial SO$_2$ oxidation process.

It was shown that the Pt/Zr-Si-GFC is capable to provide complete CO conversion in SO$_2$ presence at temperatures less 300°C, at the same time showing high resistance to deactivation.

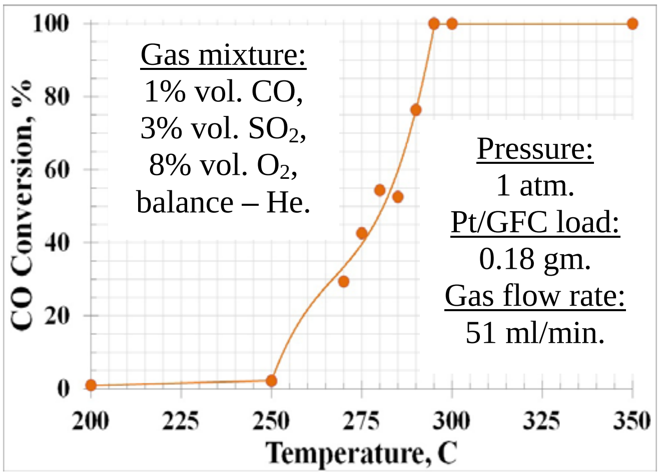

Fig. 1. CO conversion vs. reactor temperature.

Application of such catalyst in the reverse-process will allow to raise essentially efficiency of purification of waste metallurgical gases from SO$_2$ under presence of significant amounts (up to 1-2% vol.) of CO.

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PP-32

CONVERSION OF A STRAIGHT-RUN GASOLINE FRACTION OF PETROLEUM OVER ZEOLITES SYNTHESIZED IN DIFFERENT WAYS

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Introduction

Zeolite reforming make it possible to manufacture high-octane motor gasolines of various brands without blending or the addition of antiknockagents over zeolite catalysts, which do not require thorough preliminary desulfurization or hydrofining of raw materials and the use of a hydrogen-containing gas.

Experimental

The high-silica ZSM-5 zeolite used in the study had a silica ratio of 60-220 and was prepared via the hydrothermal synthesis from alkaline aluminosilica gel with hexamethylenediamine (HMDA) and ammonium bicarbonate (ABC), as an organic additive. The activity of the obtained catalysts was tested using a flow unit during the process of conversion of the straight-run gasoline fraction (IBP–180°C). The experiments were carried out at atmospheric pressure. The temperature of the process was 300–380°C. The feed-space velocity was 2 h^{-1}. The products were determined with the use of gas–liquid chromatography.

Results/Discussion

To increase the yield of the catalysis product and the concentration of hydrocarbons of the iso-branched structure in its composition, the following improvements have been proposed: the replacement of part of the aluminum cations in the zeolite framework with iron ions [1]; the preparation of zeolite catalysts with silica ratios (molar ratio SiO_2/Al_2O_3) > 100 [2]; and the mechanochemical treatment of zeolite-containing catalysts [3]. Developments related to the replacement of toxic structure-forming additives (HMDA) with more environmentally benign (ABC) in the synthesis of zeolite or the syntheses of zeolite without any structure-forming agents are promising [4]. To reduce the cost of pentasil-based catalysts, it was proposed to use a composite catalyst made from an available natural zeolite [5].

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PP-33

INFLUENCE OF PLATINUM ADDITION ON THE PROPERTIES OF GALLOALUMOSILICATE IN ETHANE AROMATIZATION

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Introduction

The process of conversion of low-molecular-weight paraffins into aromatic hydrocarbons over the catalysts based on pentacyl-type zeolites possessing a unique ability of conversion of light olefins and paraffins into high-molecular weight compounds is being extensively studied now in Russia and abroad. The aim of this work is to study the mechanisms of aromatization of ethane over a gallium-silica-alumina catalyst modified with platinum.

Experimental

Galloaluminosilicate (Ga-AS) with silica ratio 40 was prepared by the isomorphic substitution of gallium (III) for silicon (IV) in the zeolite during hydrothermal synthesis. Then galloaluminosilicate was impregnated by an aqueous solution of platinumhydrochloric acid (the weight fraction of platinum was changed from 0.05 to 0.5%).

Conversion of ethane was carried out in a flow type installation equipped with a quartz reactor under atmospheric pressure, at the reaction temperature 500-650 ^{o}C and a feed space velocity of 500 h^{-1}. The reaction products were analysed using gas chromatography.

Results/Discussion

The original Ga-AS exhibits a relatively low activity in the conversion of ethane into aromatic hydrocarbons. The degree of conversion of ethane over Ga-AS and the yield of aromatic hydrocarbons at 600 °C are respectively 24.1 and 15.8%. Modification of galloalumosilicate with platinum results in a significant increase in the conversion of ethane and the yield of aromatic hydrocarbons. Thus, due to the introduction of 0.05% Pt into Ga-AS the ethane conversion increases 2 times and the yield of aromatic hydrocarbons increases 1.7 times. When the concentration of platinum in Ga-AS reaches 0.3%, its aromatization and overall activities are observed to increase further. At the reaction temperature 600 °C the conversion of ethane and the yield of aromatic hydrocarbons on the 0.3% Pt/Ga-AS sample reach respectively 63.1 and 43.6%. The increase in the concentration of platinum in Ga-AS to 0.5% reduces the catalyst activity of the in the aromatization of ethane. The Ga-AS containing 0.3% Pt exhibits the highest activity in the formation of aromatic hydrocarbons from ethane.

PP-34

NANOSTRUCTURED PtPd-ZEOLITE CATALYST FOR DEEP DESULFURIZATION OF LOW-SULFUR DIESEL FRACTION

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The Pt-zeolite catalysts are found to be excellent for hydrodesulfurization of diesel fractions with low sulfur content (less than 50 ppm) [1]. To improve the sulfur-resistance of the hydrotreating Pt-catalysts, their design has to satisfy the following requirements [2]: bimodal pore texture, two types of active Pt(Pd)-sites, and optimal proton acidity.

The current communication will be devoted to study of the catalytic properties and sulfur-tolerance of Pt(Pd)-zeolite catalyst in deep desulfurization (HDS) of straight-run and secondary diesel fuel with sulfur content up to 2000 ppm as function of the catalyst proton acidity and morphology of Pt(Pd) particles.

It was shown that the Pt(Pd)-zeolite catalyst demonstrates high efficiency in deep desulphurization of low-sulfur straight-run diesel fuel at 280-320^{o}C (Table), has moderate activity in aromatic hydrocarbons hydrogenation. The catalyst provides also a decreasing of sulfur content in secondary diesel fraction, containing SRDF with gasoil of catalytic cracking and coker (70/15/15), for example at 280^{o}C from 2000 ppm to 175 ppm S. The catalyst has high sulfur-resistance and does not change of its catalytic properties after regeneration.

The good catalyst performance and high sulfur-resistance can be explained by the optimal design of bimodal pore structure, with meso- and micropores, in which two types of Pt(Pd) particles are located. The Pt-Pd states are Pt-Pd-alloy, $Pt^{\delta+}$ and PdO.

Table *Performances of Pt(Pd)-zeolite catalysts in HDS of straight-run diesel fraction and secondary diesel fraction*

Characteristics	Fuel 1 SRDF	HDS Product at temperature, ^{o}C			Fuel 2	HDS Product at temperature, ^{o}C	
		320	300	280		320	280
Density, d_4^{20}, kg/m^3	847	844	844	843	854	840,6	849
Simulated distillation, ^{0}C, 10 %	210	78	184	205	230	210	207
96 %	353	348	355	351	365	352	350
S content, ppm	1065	50	45	35	2002	225	175
Aromatic CH content, wt %	20	17	14	9	27	21	19
Cetane number	45	42	42	43	43	41	44

Acknowledgement. This study was supported by SB RAS (Grant №118)

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PP-35

PHENOMENA UNDER ILLUMINATION OVER TITANIA PARTICLES PRODUCED BY GRINDING OF RUTILE CRYSTAL UNDER AMBIENT AIR

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It is known that powdered samples of metal oxides having more fine crystal structure of nanoparticles exhibit a tendency to larger a photocatalytic activity (Boudart). For example, titanium dioxide prepared by the plasmatrone method (P25 from Degussa) has nonporous structure and consist of rutile and anatase. Such P25-Degussa is better photocatalyst than rutile or anatase or a mixture of rutile and anatase having high porosity and high specific area. Moreover photoelectric effects and photoelectrochemical efficiencies amount to maximum values for crystalline samples of TiO_2, ZnO, SnO_2 (Fox, Dulay). The powder of crystalline microparticles may be prepared from metal oxide crystals.

The rutile crystal obtained by Czokhralski method cleaved and grinded in a corundum mortar. The specific surface of TiO_2 was equal 1,6 m^2/g. Before studies of oxygen photoadsorption and carbon dioxide photodesorption only the vacuum degassing at room temperature was performed. In gas phase and on the titanium dioxide surface the water molecules were always present during measurements.

The quantum yield quantities and spectral dependencies of oxygen photoadsorption and carbon dioxide photodesorption on titanium dioxide were determined. The quantum yields amounted to following values:

a). surface absorption region (465 nm) -- 0,7 % (O_2), 0,35 % (CO_2);
b). band to band absorption region (340 nm) – 0,75 % (O_2), 0,55 % (CO_2).

Also, the photochemical activity of industrial and laboratory preparation TiO_2 was investigated. The oxygen photoadsorption quantum yields over industrial TiO_2 were equal:

a). surface absorption region (465 nm) -- 0,03 %,
b). band to band absorption region (340 nm) – 0,15 %.

Closely approximating to these values the quantum yields were stated over titanium dioxide obtained by a laboratory preparation.

The mechanism of photoprocess activity increasing under illumination from the surface absorption region was suggested. It is concluded that the photochemical activity under tropospheric solar irradiation (λ>300 nm) over titanium dioxide, produced by fine grinding of rutile crystal under ambient air, is essentially higher than the photochemical activity on titanium dioxide prepared in traditional ways.

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PP-36

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

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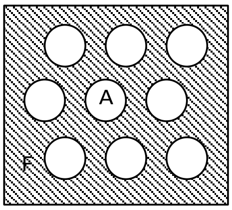
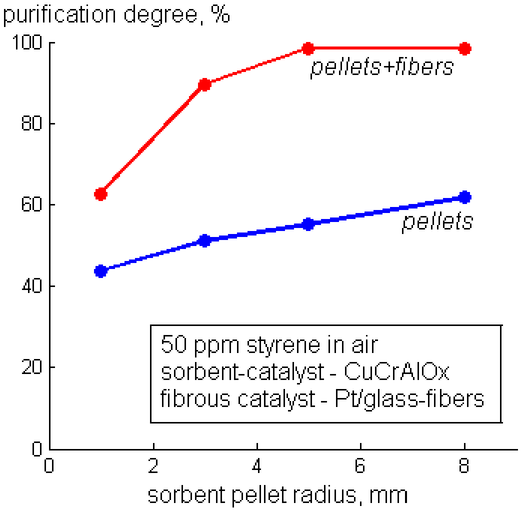
Adsorption-catalytic process for abatement of volatile organic compounds (VOC), including adsorption of VOC at the catalyst surface at ambient temperature with periodical incineration of accumulated VOC at elevated temperature [1-3], is a promising energy-saving technology for purification of lean industrial 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 (A) and of catalytically active micro-fibers (F) 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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PP-37

METHODS TO INCREASE THE STABILITY OF THREE-WAY CATALYSTS FOR EXHAUST GASES AFTERBURNING

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The problem of air pollution becomes more and more acute nowadays. Atmosphere is poisoned by toxic impurities such as NO_x, CO and hydrocarbons, which main sources are the automobile engine exhaust gases.

Catalytic on-board aftertreatment system (convertor) is already used widely in many countries to reduce the level of toxic compounds released with exhaust gases. During the working cycle automotive convertors are exposed to rather high temperatures and sudden temperature oscillations which may lead to quick deactivation of catalyst. At temperature of 900°C and above the alumina surface area drops down, and the sintering of noble metal particles (Pd, Pt, Rh) occurs, too. Both processes result in catalytic activity decline. Dispersed Pd particles readily undergo sintering into agglomerates; rhodium gets oxidized from Rh^0 to Rh^{3+} state followed by diffusion of the Rh^{3+} ions into the support bulk [1].

This work was dedicated to the synthesis and investigation of three-way catalysts based on Pt metals that possess the superior chemical and thermal stability. According to literature data [2], bimetallic Pd-Rh or Pt-Rh system is more stable and catalytically active than the corresponding monometallic ones. In this work, bimetallic Pd-Rh alloy particles were synthesized by deposition on support. The catalyst containing Pd_xRh_{1-x} (x=0.5, 0.6) solid solution as an active component was shown to be both thermally and chemically stable under red-ox conditions. Rh involved into structure of solid solution cannot be easily transformed into Rh^{3+}. It has been elucidated that the formation of Pd-Rh alloy particles on the catalyst surface prevents Rh diffusion into the bulk of support. In addition, Pd-Rh alloy species are more stable towards aggregation and sintering. The results presented in this work also suggest that catalytic performance of the resulted catalyst strongly depends on preparation procedure.

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PP-38

ZEOLITES: ADSORBENTS, SUPPORTS AND MODIFIERS IN MOLECULAR GAS CHROMATOGRAPHY

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Zeolites of types 13X (NaX) and 5A (CaA) are most useful among other zeolites in adsorption gas chromatography. The chemical nature of their surface is determined by an excess positive charge. It is the result of partial compensation of positive charge, located on a small exchange cations, for the large $(AlO_4)^-$ anions of the zeolite skeleton. Such surface is decsribed as quite definite ability for intermolecular interaction with adsorbate molecules and accordingly for elution order of the mix components. Thus, unsaturated hydrocarbons with the same C-atoms in their molecules are retained stronger than saturated ones. And they are retained the stronger than more unsaturating in the molecule of sorbate.

The single type of intermolecular interaction of zeolites restricts their field of application in practical chromatography. Moreover their application as bulk packings in chromatographic columns is often impossible because of their high adsorption surface potential and the consequent strong retention of most of compounds, including unsaturated compounds. As result, they are mainly useful for separation of simple gaseous mixtures, for example, hydrogen, oxygen, nitrogen, methane and carbon monoxide.

The field of zeolite application can be significantly extended by using them **(a)** as a support, and **(b)** as a modifier. As far as modified zeolites are concerned, data on their preparation and systematic gas chromatographic investigation are very limited and insufficient, with more information available on the surface-layer adsorbents. The last ones can be obtained by coating zeolites as an adsorbent surface layer on an inert macroporous support such as diatomaceous earths (Chromosorb W or P, Chromaton, Porolit, Tsvetochrom). Adsorption processes occur in such packings only in the surface layer of small depth equal to the thickness of the active sorbent layer. This allows substantial reduction of the retention values and consequently the chromatographic analysis time.

The results of investigation and application of zeolites as: a) support modified by carbonization and b) modifier coated as a porous surface-layer on diatomaceous earths are presented in this study. They showed the carbonization to lead to a change of their chemical surface nature and in some cases of their molecular-sieving characteristic. Unlike the initial zeolites, adsorbents obtained in this way combine the surface properties of both the initial zeolite and of carbon-containing materials. They were used in analysis of the trace amounts of carbon monoxide not only in air but also in hydrogen-containing mixtures formed in its synthesis.

Porous layer adsorbents synthesized on base of zeolites were used in gas chromatography analysis of the reaction mixtures, analysis of which was a problem or was impossible with traditional chromatographic materials and even with capillary porous-layer columns. Among these reaction mixtures were, for example, the feeds formed in coarse of catalytic reaction of oxygen-free methane dehydrocondensation.

As compared with well-known materials (carbons, organic porous polymers), zeolites, modified and supported as a thin porous layer, are characterized by more selectivity to separate light boiling compounds formed in catalytic reactions. They permit to reduce the temperature of analysis and the chromatographic analysis time, for example, of the feeds (air, propane, propylene, acetylene and methylacetylene) of catalytic propylene cleaning.

The separation properties of zeolite-based adsorbents are compared with those of various chromatographic materials characterized by different chemical surface nature as well as their adsorption textures.

PP-39

PREPARATION AND PROPERTIES OF ZrO_2-Al_2O_3 MATERIALS

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Microporous zirconium-alumina materials (ZrO_2-Al_2O_3) with structure of bayerite have been synthesized using Keggin type cation $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ and $ZrOCl_2$ as Al and Zr source Textural and physicochemical properties of these materials ZrO_2-Al_2O_3 samples were characterized by N_2-adsorption/desorption analyses, X-ray diffraction, FT-IR and ^{27}Al NMR(MAS), FT-IR spectroscopy using pyridine, PhCN and $CDCl_3$ as probe molecules. It was shown that textural properties of ZrO_2-Al_2O_3 samples can be controlled by the Zr content in Zr,Al-solution (Zr/Al = 0 – 1 mol/mol). According to DR-UV-vis spectroscopy the increase in Zr content in sample favours the formation oligomeric ZrO_2 clusters. Two types of Lewis acid sites were founded by FT-IR spectroscopy using PhCN as probe molecule. There are strong Al-Lewis acid sited generated by coordinative unsaturated Al ions and weak Zr-Lewis acid sites generated by coordinative unsaturated Zr ions. The increase in Zr content into clay leads to the decrease in amount of Al-Lewis sites and increase in Zr-Lewis acid sites.

ZrO_2-Al_2O_3 materials have been tested as catalysts for alcohols oxidation (benzyl alcohol and cyclohexanol) with H_2O_2. The activity of ZrO_2-Al_2O_3 was found to increase with increase in Zr content. Data of ^{27}Al NMR(MAS) and FTIR spectroscopy point to the existence of several sites of Al-OH. Al–OH groups of the type I with a weak and moderate acid strength are the active sites for the alcohol oxidation. At the same time Al–OH groups of the type II with a strong acid strength are the active sites for decomposition of H_2O_2.

Headings: **Structured catalysts for chemical processing and environmental protection**

PP-40

APPLICATION OF XAFS SPECTROSCOPY TO STUDYING PERSPECTIVE NANO-DISPERSED GOLD CATALYSTS

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It is well know that metallic gold due to its electronic structure is most inert among noble metals, nevertheless nano-dispersed gold forms located on oxide supports may be used as very active catalysts for numerous industrially important reactions. These systems are very promising for complex organic synthesis, for instance for selective isomerization of linoleic acid for CLA (conjugated linoleic acids) production and for processes of environmental catalysts, such as, CO oxidation and selective oxidation of secondary alcohols. This work is devoted to a detailed structural study of the nano-sized gold stabilized forms located on oxide supports by XAFS spectroscopy. Reliable analysis of the nature of gold forms is extremely important for design of new effective gold based catalysts for different industrial applications. Synthesis of low-percentage (~1-3% Au) samples was carried out under varying preparation methods (impregnation, deposition-precipitation with urea, direct ion exchange), calcination temperatures and activation methods (modifications of oxide support by Zr and Ce oxide compositions). All XAFS spectra of the Au–L_3 edge were recorded at Siberian Synchrotron Radiation Center (SSRC, Novosibirsk). The local gold arrangements and the state of metal component of the prepared catalysts were studied. The interatomic distances and corresponded coordination numbers were established. All possible structural models were discussed. It was shown that different stabilized gold forms located on oxide supports were formed, most probably depending on a sample prehistory: Au(3+) cations (having octahedral oxygen surrounding), gold nano-clusters ~10Å and gold metallic nanoparticles ~20-100Å. Some correlations between catalytic activities and structural functional properties of the studied samples were found. Additionally samples of catalysts were characterized by the TEM, EDX and XPS methods. The data obtained by all the methods are in a good agreement.

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PP-41

APPLICATIONS OF XAFS SPECTROSCOPY FOR STUDYING OF NANO-SIZED CATALYSTS USED FOR SYNTHESIS OF BIOFUEL COMPONENTS

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Recently great attention is attracted to development of highly effective approaches of converting renewable biomass into energy resources as biofuels. Some spirit compounds, such as ethanol, butanol, pentanol, glycerine, being biomass fermentation products, may be used as fuel components, both without any treatment and after catalytic converting, that provides production of more effective fuel components.

This work is devoted to a study of the local structure of original nanosized catalytic low-percentage systems W(Ta)-Re/Al_2O_3 and Pd-Zn/Al_2O_3, used for production of alkanes or olefins fractions C_4-C_{12+} which components of biofuels obtained from biomass fermentation products. Initial samples of catalysts were prepared by zol-gel method from original mono- and hetero-metallic precursors [1, 2] impregnated on the γ-alumina oxide. All EXAFS and XANES spectra of the W(Ta)-L_3, Re-L_3, Pd-K, Zn-K edges were recorded at Siberian Synchrotron Radiation Center (SSRC, Novosibirsk).

Genesis of the local structure of the studied catalytic nanosystems was characterized in detail. The interatomic distances and corresponded coordination numbers were revealed. All possible structural models were discussed. Relations between their catalytic properties, local structure distortions and state of metal components were demonstrated. It was found out that active components of all studied systems were highly dispersed onto the oxide support surface and strong interaction with the support took place, resulting in formation of mixed surface MeO_x-Al_2O_3 oxides. Additionally, the samples of catalysts were characterized by the TEM, EDX and XPS methods. The data obtained by all the methods are in a good agreement.

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