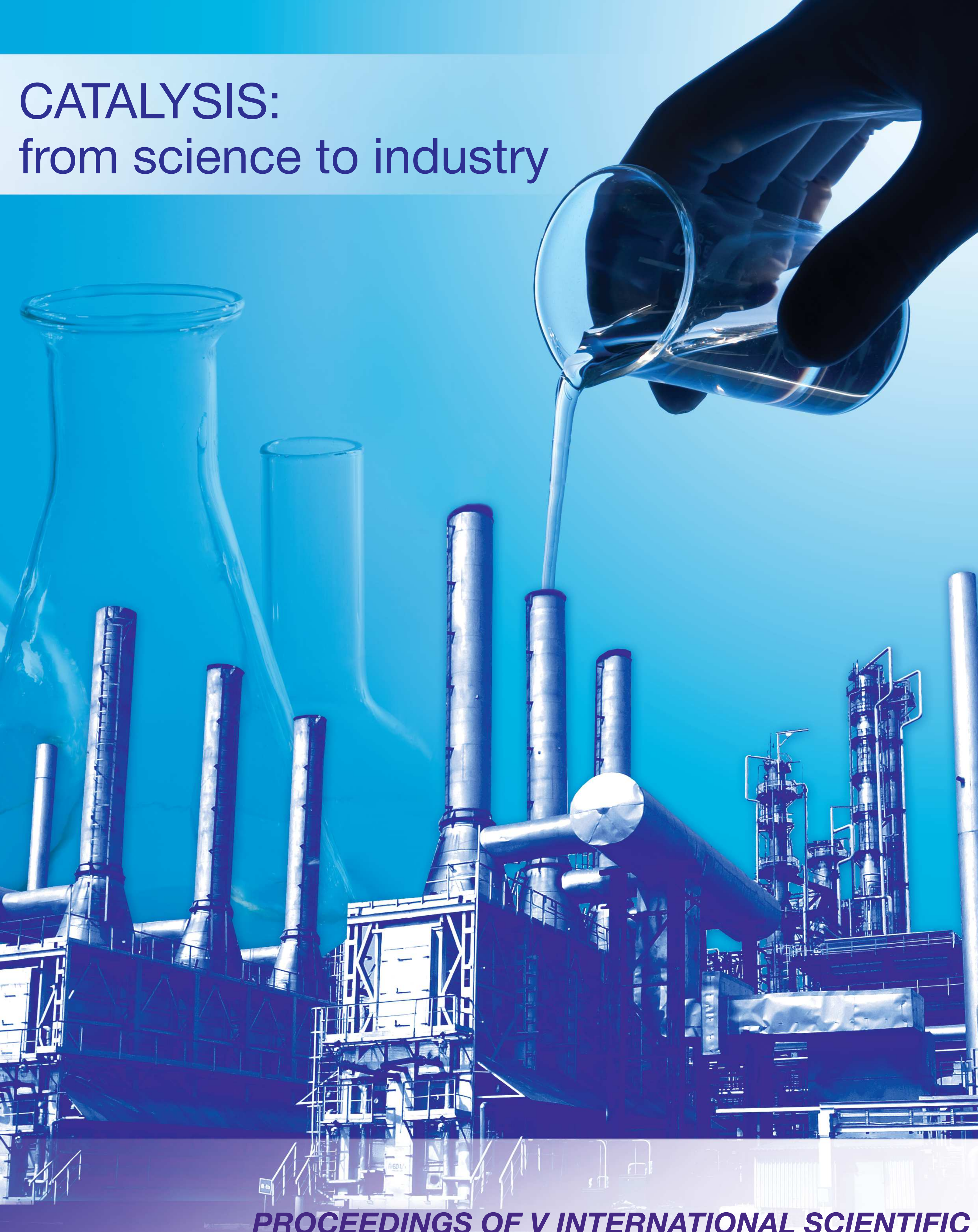
# CATALYSIS:
# from science to industry



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# CATALYSIS: FROM SCIENCE TO INDUSTRY

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# V INTERNATIONAL SCIENTIFIC SCHOOL-CONFERENCE FOR YOUNG SCIENTISTS

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# PLENARY LECTURES

# Environmental TEM dynamic high spatial resolution studies of surface mobility on ceria nanocubes and of metal/ceria supported catalysts evolution during redox cycles

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Ceria is, in one hand, a fascinating material from the point of view of fundamental studies and, in the other hand, a rather important material for applications in catalysis both as a catalyst and as a catalyst support. Although widely studied by TEM and despite an exhaustive literature on the structure of reactive facets of $CeO_2$ correlated to its catalytic mechanisms, the temporal evolution of the atomic surface structure exposed to realistic redox conditions together its possible influence on the supported metallic phases remains elusive.

In a first step, we provide a direct visualization of the atomic mobility of cerium atoms on (100) surfaces of $CeO_2$ nanocubes in high vacuum, $O_2$ and $CO_2$ atmospheres and by quantifying the cationic mobility, we achieved control of the surface dynamics under exposure realistic gas atmospheres, yielding new information for a better understanding of the intimate catalytic mechanisms.

In a second step we present rather morphological, structural and chemical changes on metallic catalysts supported on ceria during redox cycles. $Ir/CeO_2$ is used in the steam reforming of methane and the observed changes in size and morphology of Ir nanoparticles associated with modification of the catalytic behavior of the catalyst could be associated with the existence of a metastable iridium sesquioxide phase. We provide structural information for this phase, that has never been experimentally identified before, and for which only theoretical suggestions have been made on its structure. $Pt/CeO_2$ is used as a diesel oxidation catalyst; we evidenced a dynamic structural behavior of Pt nanoparticles on the ceria surface under reducing/oxidizing conditions at moderate temperatures (< 500°C) where redispersion occurs in oxidizing atmospheres whereas Pt nanoparticles reform under reducing conditions. A protocol was devised to control Pt particle formation and thus enhance the catalytic activity of $Pt/CeO_2$-based exhaust gas catalysts.

The surfaces of $CeO_2$ nanocubes and the $Ir/CeO_2$ and $Pt/CeO_2$ catalysts were studied, within realistic gas environments well-adapted for each mentioned application, in a dedicated FEI Titan 80-300 environmental TEM (ETEM) operated at 300 kV and equipped with a Cs-image corrector, a high-speed Gatan CMOS OneViewTM camera, an Oxford Instruments SDD XMaxN EDX spectrometer and a Tridiem ERS Gatan Imaging Filter (GIF).

*The author warmly acknowledges the invaluable contributions of T. Epicier, M. Bugnet, L. Roiban (MATEIS, F) and M. Aouine (IRCELYON, F) to the ETEM study and F. Meunier, P. Gélin, L. Massin, P. Vernoux, S. Loridant, C. Geantet, G. Ferré (IRCELYON, F) and A.M. Gänzler, M. Casapu, J.D. Grunwaldt (KIT, D) for the supported catalysts preparation and fruitful discussions.*

# The active sites in metal-oxides systems for oxidative catalysis

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Theoretical ideas about the action of heterogeneous catalysts of various types underlie all practical developments and technologies of catalysis. The most important area of theoretical concepts is the development of fundamental aspects on the nature of active sites of catalysts that provide the most effective routes for the formation of target and useful products.

In heterogeneous oxidative catalysis for the formation of active sites, one of the most effective pathways is the strong chemical interaction of metals and oxides in their nanostructured state. In this case, it is possible to form various heterophase and heterogeneous structures capable of providing both partial and complete oxidation. For complete oxidation, such structures and states of the active sites are necessary, which would be able to provide low-temperature oxidation, while maintaining high thermal stability and catalytic activity in the presence of potential catalytic poisons.

In this lecture, mechanisms for the formation of active sites in metal oxide systems will be considered using the example of PGM-Oxides (PGM - platinum group metals Pt, Pd, Rh; oxides - $Al_2O_3$, $CeO_2$) [1-13]. Various factors that play a primary role in the formation of efficient oxidation centers, such as the redox properties of oxides, the dispersity of oxides and PGM, the charge states of the components will be considered in the work. The great attention will be paid to the problem of interaction of PGM with the surface of oxides and the establishment of PGM forms responsible for the main stages of the catalytic cycle of the oxidation reactions. In addition, the lecture will emphasize the problem of establishing correlations "the structure of the active site - the activity of the catalyst" with the use of modern physicochemical methods for studying the composition and structure of both the bulk and surface of the catalysts, as well as the reactivity of the reagents.

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# Using $CO_2$ to produce olefins by oxidehydrogenation

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Nowadays dehydrogenation of light ($C_3$-$C_4$) alkanes is the process of choice to get high purity olefins as building blocks for petrochemical processes. But due to its endothermicity, dehydrogenation faces the thermodynamic limitations, that increase with the decrease of the chain length, specially for ethane, and suffers of catalyst deactivation by coke formation. Aerobic oxidative dehydrogenation (ODH) is exothermic and avoids such limitations and prevents coke formation, but faces overoxidation of the produced olefin, which limits its selectivity, the key parameter for practical application [1]. The use of $CO_2$ as an oxidant softer than oxygen may contribute to avoid this problem.

Though it is endothermic, ODH with $CO_2$ ($CO_2$-ODH) may be more selective and also might contribute to reduce $CO_2$ emissions, while its subproduct as oxygen donor, CO, is a valuable feedstock, what contribute to the overall atom sufficiency for the process [2]. In addition, $CO_2$ can contribute to the removal of coke, thus increasing the catalyst stability.

Since the pioneering work of Krylov's group using transition metal oxides [3] two main types of oxide catalysts have been reported for this reaction. On one side, those based on typical dehydrogenation catalysts, such as chromia-based ones. On the other, ceria-based catalysts, first reported by our group [4], includng those based in ceria-zirconia.

The role of $CO_2$ in these dehydrogenation reactions has been matter of controversy, as it can be dual: acting as a true oxidant or as an oxygen scavenger, shifting the dehydrogenation equilibrium (also named combined route). The prevalence of the oxidative or the combined route depends mostly on the nature of the active oxide component and its interaction with $CO_2$, in other words, if $CO_2$ can reoxidize the reduced oxide, as we have shown this is the case with ceria-based catalysts.

The features of each type of catalyst and their differences, the effect of the catalyst characteristics on the reaction and its interaction with $CO_2$, the effect of small addition of oxygen in the feed to balance the endothermic energy demand, and the current state-of-art will be revised and discussed, with special attention to recent studies on the role of different oxidants in defining the chromium oxidation state in $Cr/SiO_2$ catalysts [5], and the effect of support on the chromium state and the catalytic performance [6].

The use of $CO_2$ in these reactions looks very promising, though further studies are needed to overcome the issue of catalytic activity stability in the long term, the improvement of activity to reduce the reaction temperature range to be used, and, probably, the integration of energy transfer with some exothermic reaction, to balance the endothermicity of these reactions.

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# Development of physical and chemical basis for the synthesis of microspherical alumina carriers in hydrothermal conditions for fluidized bed catalysts

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Microspherical catalysts of the fluidized bed are widely used in petrochemical processes of dehydrogenation of lower paraffins and oxidative chlorination of ethylene. The production of dehydrogenation catalysts is the most large-tonnage. Only PJSC Nizhnekamskneftekhim jointly exploits up to 5800 tons per year of the IM-2201 catalyst obtained by spray drying the catalyst slurry and 2800 tons per year of the new generation impregnation catalysts obtained by depositing the active components on the alumina carrier. In this case, the carrier determines the following important characteristics of the catalyst: the strength of the granules and their resistance to abrasion, which affects the catalyst consumption per ton of the product obtained; granulometric composition providing the required hydrodynamics of the fluidized bed and abrasive activity with respect to the walls and internal structures of industrial reactors. The acid-base properties of the carrier surface significantly influence the activity and selectivity of the catalyst, which ultimately determines the cost of the monomers and synthetic rubbers produced.

The physicochemical basis for the synthesis of microspherical alumina carriers obtained by hydrothermal treatment of the products of gibbsite thermal decomposition and the method for obtaining microspherical alumina carriers by thermal decomposition of gibbsite agglomerates and hydrothermal processing of the products obtained, which allows to regulate the phase composition, structural and physico-mechanical characteristics of boehmite carriers and aluminum oxides on and basis are developed based on the systematic studies carried out.

Microspherical boehmite and alumina carriers with high mechanical strength, thermal stability, low abrasive activity and low acidity of the surface and fluidized bed catalysts (dehydrogenation of isobutane, isopentane) on their basis are developed.

The technologies of obtaining microspherical boehmite carrier and catalysts for the dehydrogenation of isobutane and isopentane on the basis with a capacity of 1000 tons/year were mastered at JSC Karpov Chemical Plant (Mendeleevsk) and 2000 tons/year at PJSC Nizhnekamskneftekhim (Nizhnekamsk).

Experimental-industrial tests of the microspherical alumina chromium catalyst of KDI grades (TU 2173-075-00206457-2007) and KDI-M (TU 217341-001-02066730-2014) on the technological lines of dehydrogenation of isobutane and isopentane in PJSC "Nizhnekamskneftekhim" were carried out. Based on the results of pilot tests, the catalyst showed high activity and selectivity, reduced consumption per ton of olefins produced in the dehydrogenation of isobutane and isopentane.

# Chemical looping

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During the twenty century chemists have developed efficient chemical reactions for converting fossil resources into a broad range of chemicals and fuels, and this can be considered one of the most important and far-reaching scientific developments. Today, essentially all transportation fuels are refined in a number of catalytic processes and most chemicals are also produced using technologies based on catalysis. A few well-known examples illustrate the impact: about half of all petrol in the world is now produced by fluid catalytic cracking using specially designed zeolite catalysts, and the Haber-Bosch process - featuring an iron catalyst - continues to have a key role in the production of fertilizers. The list of important small- and large-scale processes by which fossil resources are converted into fuels and chemicals is almost endless.

Such catalytic technologies have also resulted in various environmental issues — even the best processes do not allow a complete elimination of undesirable byproducts. Many innovative, catalytic technologies have subsequently been implemented to remedy these new problems; one famous example is the precious-metal-based three-way catalyst installed in most petrol-fuelled passenger cars. Moreover, these developments have contributed to an increased use of fossil resources and thus to the increasing carbon dioxide levels in the atmosphere. Currently, there is a significant drive to relinquish our dependence on fossil fuels and to minimize the emission of carbon dioxide. Clearly, this calls for many new and improved catalytic processes, and for catalytic technologies that focus on prevention rather than on remediation.

If we are honest, currently there is no efficient technologies exist that enable the use of $CO_2$ as a starting material. This could serve the dual purpose of producing value added chemicals using $CO_2$ as a $C_1$ base chemical at the same time reducing $CO_2$ emissions. If this could be carried out at large scale (megaton) than this would definitely help to mitigate the effects of climate change by recycling part of the waste $CO_2$ while creating new opportunities for the chemical industry, making it one of the top research priorities of the EU to reach its 2050 climate objectives in a cost-effective way. What to do? As usual the solution is very close but we don't see it. Chemical looping is one of several emerging technologies capable of low-emission with application in production of heat, fuels, chemicals, and electricity. This technology is rapidly becoming an established "clean combustion technology" due to its highly efficient inherent $CO_2$ capture. I would like to demonstrate that chemical looping has large potential well beyond combustion as a flexible platform technology for process intensification. The flexibility of the looping platform is a result of the fact that a single reaction is broken down into two, spatially or temporally separated half-reactions coupled through the transport of a "carrier" material, thus opening up a wide parameter space for design and optimization of reactor feed, materials circulation, and process operation. The chemical looping principle should be fundamentally applicable to any catalytic reaction, with suitable materials that allow transport of the desired functional group. When applied for thermodynamically limited reactions, the shift of equilibrium to the products' side according to the Le Chatelier's principle allows not only product separation, but also higher conversion levels and efficient heat integration, and leads to less complex separation trains and higher efficiency [1,2].

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# New Trends in Propylene Production Technologies

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Propylene is the basic component in modern industrial petrochemical and organic synthesis. There is an increasing worldwide demand for propylene due to a higher demand for polypropylene than polyethylene. Also the necessity for propylene is rapidly increasing due to the increasing demand of propylene oxide, oxo alcohols, acrylonitrile, cumene, etc.

Pyrolysis and catalytic cracking, which account for ~80% of the world production of propylene, are the major source of worldwide propylene raw material. But these processes can't fully satisfy the growing demand for propylene on the petrochemical market. The new propylene production technologies as a main product are required. Now catalytic pyrolysis, deep catalytic cracking, propane dehydrogenation, metathesis of ethylene and 2-butenes are applied for increasing of propylene production.

The current industrial and promising technologies and methods for the preparation of propylene from oil and gas raw materials, including combined processes, and processes based on biological raw materials were considered. Pyrolysis of hydrocarbon raw materials remains the main industrial process for the worldwide propylene production. Pyrolysis of light gas raw materials is a global trend towards improving the economic effect of process, but leads to a reduction in the propylene yield. The propylene production can be increased by using the combination of pyrolysis with metathesis and direct conversion of ethylene to propylene. Such a combination of technologies allows for flexible regulation of the ratio of produced monomers and corresponds to the market situation of their consumption.

The use of ethylene as the sole source for the production of propylene allows one to adjust the ratio of the monomer products and conform to the market conditions and consumption. The technology for producing propylene from ethylene consists of two stages. The first stage is dimerization of ethylene into butene-1. The second is isomerization of butene-1 into butenes-2 and the third is metathesis with ethylene. However, direct conversion of ethylene to propylene as a one stage process is the most desirable route, since this process consists of a simple hardware design that reduces capital and operating costs. The development of a one stage process for the production of propylene from ethylene is aimed at seeking an effective multifunctional catalyst that provides the implementation of the appropriate reaction routes.

In the coming years, the capacity of deep catalytic cracking of heavy oil fractions, residual and by-products of hydrocarbon raw materials will increase even more. This process gives high propylene selectivity, and therefore it can be expected that this process will soon become the main for industrial petrochemical and organic synthesis.

Propane dehydrogenation is used in industry less often than pyrolysis. Perhaps this is due to the fact that the same raw materials are used for these processes. Providing very high selectivity, propane dehydrogenation is optimal for industrial enterprises, products of which are mostly based on the use of propylene as a starting raw material. Light alkanes as a gas raw materials are significantly increases the profitability of propylene producing, and also allows solving environmental problems for utilization of associated petroleum gases.

The propylene production from natural gas today has no prospects for use on a large scale in industry because of high capital and maintenance costs of production, primarily for stages of preliminary syngas production and its conversion into methanol or DME. Direct conversion of natural gas into propylene requires development. The propylene production from biological raw materials is not expected because of their substantially higher cost compared with that of oil feedstock and limited availability in some countries.

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# Structure activity relationship in Ni based catalysts for dry reforming of methane

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Methane and $CO_2$ are the most abundant greenhouse gases and are the main contributors to the recent climate-change issues. The dry reforming of methane (DRM) is a chemical process that consists of converting methane and $CO_2$ to syngas with a $H_2$/CO molar ratio of 1 [1]. As a result, this process has the potentials to mitigate the environmental challenges associated with greenhouse gases emissions and to convert biogas and natural gas to syngas [2]. The syngas obtained is convenient for the production of hydrocarbons via Fischer-Tropsch reaction and for the synthesis of oxygenated chemicals [3].

Being an extremely endothermic reaction ($\Delta H_{298K}$ = +247 KJ $mol^{-1}$), DRM requires high operating temperatures, usually in the range of 900–1273 K, to achieve the desirable conversion levels.

Despite its considerable environmental potentials, DRM is not considered an industrially mature process. The extremely high endothermic reaction, coupled with rapid carbon formation leads to the catalyst deactivation. Therefore, the design of new efficient and stable catalysts is still challenging.

Nickel is the most frequently used metal in DRM because of its good catalytic activity and its cost-effectiveness as compared with Pt, Ru or Rh-based catalysts [4]. However, the formation of significant amount of carbon coke and the particle sintering at the high temperature limit its applications. The addition of second noble metals, such as Au, Pt, Pd may reduce poisoning and deactivation [5, 6]. Other solution to improve Ni catalysts lifetime is to dope with second transition metals, like Co, Fe, able to stabilize Ni as alloyed nanoparticles with enhanced resistance to coke poisoning [7]. Moreover, natural materials such as clays, phosphates and volcanic rocks are often added to Ni catalysts formulations [8].

In the present work, the performances of different catalysts used in DRM are discussed and the effect of active metals, supports and promoters are investigated for a better understanding of catalyst design.

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# Catalysis as the cornerstone of green chemistry

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Green chemistry approach plays the key role in the technical aspect of the sustainable development. Only on this basement 17 UN Global Goals to Transfer Our World adopted in 2015 [1] can be realized. Nearly all of these goals relate to the development of chemistry, directly or indirectly, and cannot be achieved without the use of green chemistry approaches. Thus, green chemistry is the basement to meet the goals: 1 – no poverty, 2 – zero hunger, 3 – good health and well-being, 6 – clean water and sanitation, 7 – affordable and clean energy, 8 – decent work and economic growth, 9 – industry, innovations and infrastructure, 11 – sustainable cities and communities, 12 – responsible consumption and production, 13 – climate action.

Catalytic processes constitute the very essence of green chemistry. Their great variety, high selectivity and atom economy provide means to solve many technical problems faced by chemists on the path to the sustainable development.

This lecture will elucidate great possibilities provided by catalysis in the fields of energy production, biomass transformation to valuable chemicals, special chemicals production etc.

Some urgent topics of green chemistry from the perspective of catalysis will be briefly characterized, which relate to:

- the substitution of rare and precious elements with those which are common on Earth in catalysts compositions;
- the estimation and decrease of toxicity of the chemicals used for catalysts preparation, or as raw materials in catalytic processes under development;
- the life cycle analysis providing valuable instrument to compare competing catalytic processes in a reliable and convincing way;
- a comparison of end-of-pipe technologies and new production ways for minimization of wastes;
- the use of biologic objects as prototypes and raw-materials for catalysts preparation.

The set of examples demonstrating innovations in the fields listed above will be presented.

Special attention will be given in the lecture to the need in holistic approach to differentiate “green” and “not green” processes instead of attribution the processes as green on the base of the only one characteristic feature e.g. the use of ionic liquid or supercritical fluid as a solvent.

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# Catalytic conversion of bioderived components over bifunctional catalysts

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Catalytic transformation of biomass derived components, such as, carbohydrates, terpenoids, fatty acids, and polyphenols into valuable chemicals and fuels is one of the most relevant research areas being important for both academia and industry [1,2]. For the latter it is a challenge to find alternative syntheses for substances that are currently obtained starting from crude oil. The challenge, that might also be an opportunity, is related to different feedstock properties. Biomass consists of highly oxy-functionalized molecules from which oxygen should be removed, especially if fuels are the desired products. For chemicals, alternative synthesis might be possible that might even be more economical [3-5].

Mono-functional catalysts used for transformations of bioderived components often cannot exhibited the behavior required for multiple-step reactions of biomass valorization through e.g. dehydration, aldol condensation, ketonization, amination, decarboxylation, etc. Bifunctional solid catalysts allow carrying out cascade/tandem/sequential-type reactions in a single pot, lowering or even eliminating isolation or purification steps [6]. Several examples from our recent studies will be given for multiple transformations of such biomass derivatives into valuable biofuels and related chemicals over bifunctional catalysts realized in one-pot mode.

Combination of valeric acid synthesis from levulinic acid with efficient ways of producing the latter, opens new opportunities for synthesis of valuable compounds for transportation sector from valeric acid [7]. Consecutive decarboxylative coupling (ketonization) and ketone hydrodeoxygenation in a single reactor over one catalyst bed will be given as an example. Key factors influencing both ketonization and hydrodeoxygenation as well as their mutual influence will be clarified to provide insights for design of more efficient one-pot catalysts. Emphasis will be placed on optimal combinations of hydrogenating (VIII group metal) and hydrodeoxygenating (metal oxide) functions as well as mechanistic aspects elucidated by DRIFTS [8, 9]. Another example is related to one-pot synthesis of complicated amines by monoterpene alcohol amination with myrtenol and aniline as substrates [11-13]. These amines exhibit specific physiological properties and can be used as intermediates of potential drugs for neurological diseases [10]. Gold catalyst activity and product distribution were shown to be strongly dependent on the support nature, correlating with the acid-base properties of metal oxides. Basic sites on the metal oxide surfaces are needed for the initial alcohol activation, while protonic groups on the support are essential for formation of the desired amine. The highest activity in one-pot myrtenol amination among the tested catalysts was obtained over Au/$ZrO_2$ bearing both acidic and basic surface sites.

Overall appropriate bifunctional catalytic materials provide many opportunities for design of highly efficient reaction systems for production of biofuels and chemicals from lignocellulosic biomass.

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# KEYNOTE
# LECTURES

# The influence of the metal complex – support interaction on the formation of platinum centers in Pt/Al(Mg)O catalysts

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The properties of the supported metal catalysts are largely determined by the size, morphology and electronic state of the metal particles, and the formation of these characteristics often depends on the processes occurring in the early stages of preparation. These include the precursor of the active component formation, the nature and strength of its interaction with the support and sequential transformation on the surface at various stages of synthesis. In the present work, the role of the nature of the active metal precursor and the interaction of the metal complex-support is demonstrated by examples of the formation of platinum catalysts using supports containing aluminum atoms: alumina, AlMg(M)$O_x$ mixed oxides obtained from layered double hydroxides (LDH), and also alumina modified by synthesis of MgAl-LDH on its surface.

Detailed study of the composition and properties of chloride Pt(IV) complexes adsorbed on gamma-alumina showed that two mechanisms of the metal complex – support interaction can occur: electrostatic adsorption with platinum fixation as outer-sphere complexes and coordination binding with the formation of inner-sphere platinum complexes. The realization of a certain mechanism makes it possible to form platinum particles with the necessary dispersion and electronic state and, consequently, to regulate their catalytic properties. Special methods are proposed that make it possible to realize selectively the required mechanism for platinum complexes fixing: by changing the composition of the Pt (IV) complexes and by changing the properties of the $Al_2O_3$ adsorption centers.

The use of supports with spatially ordered structure is a promising way to control the characteristics of supported metal and obtain nanoparticles with uniform properties. Such supports can be represented by layered double hydroxides. LDHs have the composition $(M^{2+}{}_{1-x}\ M^{3+}{}_x(OH)_2)^{x+}(A^{n-})_{x/n}\ nH_2O$, where $M^{2+}$ and $M^{3+}$ are bi- and trivalent metal cations, and comprise positively charged hydroxide layers and anions $A^{n-}$ located in the interlayer space. The nature of interlayer anion is an essential parameter affecting the amount of anchored platinum, the composition of surface species, and their location in the structure of layered material. A low exchange capacity of carbonate LDH toward the double-charged anionic chloride complexes of platinum made it possible to anchor platinum selectively with participation of OH groups of the hydroxide layers and adsorption of hydrolyzed inner-sphere complexes on the surface. Their reduction led to the formation of isometric platinum particles of size 2-4 nm. When platinum complexes were anchored on aluminum-magnesium hydroxide with interlayer OH–anions, the precursor was located mainly in the interlayer space as outer-sphere complexes with subsequent formation of a plane morphology particles, length of 50 nm and thickness close to interlayer distance in LDH (0.75 nm).

Structural features of oxide supports were studied by XRD (D8 Advance, Bruker). Adsorption–desorption isotherms of nitrogen at 77.4 K were measured using a static volume vacuum system ASAP-2020M (Micromeritics). Elemental analysis was made by ICP-AES on Varian 710-ES spectrometer. CO and $H_2$ pulse chemisorption (AutoChem II 2920, Micromeritics) and transmission electron microscopy (JEM-2100, JEOL) were used to estimate the particle size of platinum. X-ray photoelectron spectroscopy was carried out on a spectrometer (SPECS, Germany). EXAFS spectra were measured at the ID26-beamline of the European Synchrotron Radiation Facility. Differences in the anchoring mechanism of metal complexes on $Al_2O_3$ and LDH were revealed by $^{195}$Pt MAS NMR (Avance-400, Bruker). Reactions of alkanes dehydrocyclization and dehydrogenation were employed for catalysts testing.

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# UV-vis DR spectroscopy for analysis of electronic state of cobalt stabilized in oxygen containing systems

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The study of the electronic state and coordination environment of d elements in heterogeneous catalysts by the UV-Vis DRS method is particularly interesting, since the components of the catalysts are almost always amorphous or highly dispersed and have small concentrations of modifying components. Under these conditions, other physical methods of research are of little informative. No effects on the sample and changes in its physicochemical properties are observed at registration of UV-Vis DRS spectra, since the energy of the two radiation sources is relatively small; and the penetration depth of the beam, when analyzing the sample in the form of a powder or granules, is about a millimeter.

UV-Vis DRS allows studying both the state of the sample surface and its volume. In addition, UV-Vis DRS is ideally suited for the quantitative analysis of d elements in true solutions, which we subsequently use to prepare both massive systems that are precursors of multifunctional materials and supported heterogeneous catalysts of various chemical processes.

Using further various treatments (calcination temperature and media), it is easy to separate the d elements stabilized on the sample surface and in its volume. In the course of temperature treatments, the interaction of the d elements with the support can form new compounds stabilized on the surface of the original support. New compounds can be stabilized also in the pores of the support, for example, in the HZSM-5 channels, at the interaction of d elements with non-framework elements of the support. However, under temperature treatments, the state of d elements in supported heterogeneous catalysts cannot be changed up to a certain temperature, which indicates their stabilization in the volume of the oxygen containing systems. A further increase in the calcination temperature of the samples can lead to partial destruction of the support surface and the formation of new phases of interaction of the deposited d element with the initial support. Moreover, during the reaction, new phases of reagents interaction with d elements stabilized on the surface or in the pores of the support (in the zeolite channels) can also be formed, but without destroying the initial oxygen containing systems.

UV-Vis DRS data provides a rather complete description of the electronic state of the whole system. The basis of the electronic spectra is the absorption bands assigned to d-d transitions of d elements and charge transfer bands (CTB) of ligand-metal and/or metal-ligand. From the values of the energy of d-d transitions and CTB, it is possible to determine the degree of oxidation and coordination number of d elements, the features of the crystal field of ligands, and also the nature of the interaction of d elements with each other and with the support. Analysis of UV-Vis DRS data of d elements is well developed in physics and is presented in many monographs.

The report will present the main features of UV-Vis DRS spectra of Co2+ and Co3+ cations for oxygen containing ligands in crystalline fields of different symmetry, as well as analyze the change in the electronic state of cobalt in massive systems during the transformation from hydroxides to oxides and then to more complex two-component systems. In this case, Co2+ and Co3+ cations can be stabilized both in tetrahedral and octahedral coordination in the volume of oxygen containing systems.

Using the example of deposited systems, we consider both cobalt cations stabilized in the support volume and retaining their charge state and coordination number, and cobalt cations stabilized on the surface of support with a change in their charge state and coordination. At stabilization of cobalt cations on the support surface, they can be stabilized as hydroxides, and then as oxides at high calcination temperatures not exceeding the temperature of the support treatment. With a further increase in the calcination temperature, other UV-Vis DRS spectra are observed, which indicates the formation of new, more complex, compounds, which are the phases of interaction of the cobalt cations with the support.

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# The role of metal–support interaction in $Ag/CeO_2$ catalysts for deep and selective oxidation of organic compounds

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The metal–support interaction plays an important role in the designing of the catalysts with both enhanced activity and stability. It is known that $CeO_2$ and $TiO_2$ are more favorable supports for catalysts with the strong metal–support interaction (SMSI) due to chemical features and semiconducting properties [1]. The SMSI is connected with both changes of the structures of metal and support at the interface and a redistribution of the electronic density between metal and support (electronic metal–support interaction). These phenomena lead to the formation of defects, oxygen vacancies, local charges near the metal–interface boundary that provide an increased catalytic activity. The key challenge is to elaborate the synthesis approaches to designing the catalysts with enhanced metal–support interaction.

The present work is devoted to the designing of the $Ag/CeO_2$ and $Ag\text{-}CeO_2/SiO_2$ catalysts with controllable $Ag–CeO_2$ interfacial interaction. The co-deposition precipitation (co-DP) and impregnation (imp) techniques were used to synthesize the $Ag/CeO_2$ catalysts with different metal–support interaction. To control the interaction of Ag and ceria on the silica surface, the consecutive and simultaneous impregnation of the silica by silver and ceria precursors (corresponding nitrates) were applied. Also the impregnation of the pre-reduced $CeO_2$ or $CeO_2/SiO_2$ support with an aqueous solution of $AgNO_3$ was used. It was found that the redox reaction between the $Ag^+$ and $Ce^{3+}$ in the solution or on the surface of the pre-reduced ceria particles led to enhanced $Ag–CeO_2$ interfacial interaction. The SMSI was confirmed by the XRD (increased cell parameter of $CeO_2$), TEM (epitaxial growth of Ag particles with the size of 2-4 nm on the surface of ceria in spite of a large difference of the corresponding interplanar distances of ~25%). The predominant distribution of the Ag particles on the surface of $CeO_2$ or at the $CeO_2–SiO_2$ interface was found by the TEM HR for the $Ag\text{-}CeO_2/SiO_2$ catalyst prepared by the impregnation of the pre-reduced $CeO_2/SiO_2$ support. It was shown by Raman spectroscopy that the enhanced $Ag–CeO_2$ interfacial interaction led to an increased concentration of oxygen vacancies in the $CeO_2$ structure. The results of the TPR-$H_2$ method also confirmed the increased reducibility of the $CeO_2$ surface in the presence of silver caused by the enhanced metal–support interaction.

All this factors, namely, an increased defectiveness of ceria particles, the formation of oxygen vacancies and a high reducibility of ceria, lead to the growth of the catalytic activity in oxidation reactions. Thus, an increased catalytic activity of the $Ag/CeO_2$ catalysts with SMSI was found for low-temperature CO oxidation, soot combustion and oxidative dehydrogenation of ethanol into acetaldehyde [2]. It was shown that the distribution of Ag and $CeO_2$ on the surface of silica support influenced on the activity in ethanol dehydrogenation. The enhanced $Ag–CeO_2$ interfacial interaction in $Ag\text{-}CeO_2/SiO_2$ catalyst, prepared by impregnation of the pre-reduced $CeO_2/SiO_2$ support [3], was found, and an increased activity in oxidation was observed with maintaining of the high selectivity toward acetaldehyde.

Thus, the metal–support interaction plays an important role for $CeO_2$-containing catalysts in oxidation of organic compounds. The co-deposition, simultaneous impregnation and impregnation of the pre-reduced ceria may be used to design the catalysts with an enhanced metal–support interaction. The redox reaction between the metal precursor and $Ce^{3+}$ aqueous or surface species leads to the formation of the SMSI.

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# Colloidal and powder catalytic nanoparticles synthesis based on pulsed laser ablation

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Despite the current success of the traditional chemical technologies for the obtaining of catalytic materials, new alternative physical, biological, and other synthesis methods, and their combinations are developing recently. These works are particularly in demand for obtaining nanoscale and nanocomposite catalysts and are aimed at increasing the efficiency, reducing the price of catalysts, and at the increase of the environmental friendliness of technological processes.

Pulsed laser ablation (PLA) is one of the promising physical methods for the synthesis of catalysts. PLA in liquids is widely used as a method for synthesis of "pure" stable nanocolloids (with the subsequent production of ultrafine powders) free of impurities and precursors for use in medicine, optoelectronics, etc. [1]. The improvment of this method for increasing the productivity and degree of control of the characteristics of the product nanoparticles led to successful use it also in various catalytic applications [2].

In this work, the results are presented on the study of specificity of the nanoparticle synthesis via PLA of targets of noble (Au, Pt, etc.) and chemically active metals (Zn, Ti, Ce, Al, Sn, etc.), other inorganic materials (Si). Such nanomaterials are the basis for different nanocomposite catalysts. The influence of the reaction medium during ablation on the structure and properties of the nanoparticles obtained is considered. Some examples of the obtained materials use in various catalytic applications, including photocatalysis and model CO oxidation reactions, are given [3].

In addition to PLA in the liquid, the prospects for using the PLA method in gaseous media for the preparation of catalytically active ultrafine powders will also be discussed.

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# Oxidation of Water to Molecular Oxygen by One-Electron Oxidants as the Cornerstone of Artificial Photosynthesis and Water Splitting

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More than $2.2 \times 10^{24}$ J of solar energy arrives at the Earth's surface for one year [1]. Although energy assimilated as a result of natural photosynthesis in the biosphere is lower by five orders of magnitude, the quantity of energy accumulated in the products of photosynthesis is much higher than the annual energy requirement of humanity and comparable with the total potential of the overall proved reserves of traditional fossil fuels [2]. Among potential approaches to the use of solar energy the possibility of artificially reproducing natural photosynthesis is an area of special interest. Attention to the artificial photosynthesizing systems is related to the possibility of energy storage in the most convenient form as chemical compounds.

Natural photosynthesis occurs under the action of visible radiation, and it is a complex process, which can be reduced, as a rule, to the synthesis of carbohydrates as a result of light-stimulated electron transfer from a donor molecule in the environment to the molecule of carbon dioxide in the course of the subsequent dark stages. Approximately 3.5 billion years ago the subsequent evolution of the biosphere led to the appearance of a new kind of microorganisms – cyanobacteria or blue-green algae, which are capable of using water molecules as an electron donor to oxidize water to molecular oxygen. Green plants, which appeared much more recently, became the heirs of cyanobacteria; the oxidation of water to oxygen also occurs within the photosynthesis of green plants.

From the point of view of artificial photosynthesis a simpler system in which the following overall reaction of the complete decomposition of water into hydrogen and oxygen occurs under the action of visible light is of the greatest interest: $H_2O \xrightarrow{hv} H_2\uparrow + 0.5O_2\uparrow$.

The ancestors of the organisms that oxidize water could bind some compounds (which are capable of oxidizing water and became the basis of prosthetic group) from the aquatic environment. Our experience in the development of artificial catalysts for water oxidation showed that, undoubtedly, these prototypes were the small clusters of hydroxides of common transition metals (Mn, Fe, Cu, Co) which usually available in natural water.

This lecture surveys the most important achievements in the research and development of catalysts based on Mn, Fe, Co, and Cu hydroxides for the oxidation of water to molecular oxygen by chemical oxidizing agents obtained, for the most part, at Boreskov Institute of Catalysis, SB RAS [3]. An analysis of the results of kinetic studies on water oxidation in the presence of the above-mentioned catalysts together with data obtained by quantum chemistry methods allowed us to make a conclusion on the general nature and process mechanism both in the presence of artificial catalytic systems based on metal hydroxides and the natural enzyme photosystem II of green plants. The most important properties of hydroxo compounds responsible for catalytic activity in the oxidation of water by one-electron oxidants are discussed, and a possible reaction mechanism is considered.

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# Catalysts with low Pt-Pd content: properties and prospects of their use for diesel vehicle emission control

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The TWC catalysts for diesel engines emission control usually contain noble metals – Pt, Pd, and Rh, which have high catalytic activity in CO and hydrocarbon oxidation. In the last decade, there has been a trend of progressive alteration of the preferred loadings of Pt or Pd, depending mostly on dynamics of market-value of these metals. The catalytic systems with a low noble metal (Pt, Pd, Rh) content and their combination with transition metal oxides are shown to be attractive option for TWC perfecting, especially for close-coupled converters operated at high temperatures [1, 2]. There is a great number of data on non-additive increase of catalytic activity of noble metals combination with transition metal oxides in the oxidation of carbon monoxide and hydrocarbons [2-7].

Here, our systematic study of the two synergetic effects are reporting. The first is between Pt and manganese oxides [7]. The second is illustrated by Pd addition into Pt-$MnO_x$-$Al_2O_3$ monolithic catalysts [8]. Both allow decreasing in the total loadings of Pt and Pd down to 0.52 g/L in the monolithic catalytic system for diesel engine exhaust treatment, providing high activity in low temperature oxidation of light hydrocarbons and high thermal stability.

The catalytic activity of Pt-Pd-$MnO_x$-$Al_2O_3$ monolithic catalysts in butane oxidation and DIESEL tests depends on the Pt and Pd precursors ($H_2PdCl_4 \sim Pd(NH_3)_4(NO_3)_2 < Pd(NO_3)_2 \sim Pd(CH_3COO)_2$), their individual loadings and their ratio (Pt/Pd). For a selected Pt precursor at its content 0.17 g/L, the catalytic performance of Pt-Pd-$MnO_x$-$Al_2O_3$ catalyst improves with an increase in Pd loading from 0 to 0.35 g/L and is nearly constant at a higher Pd loading (0.70 g/L). At 400 °C the CH, CO and NO conversions on the aged catalysts with optimal Pt-Pd loading are 97.5, 99.9 and 56 %, respectively. The catalyst possesses by capacity to soot oxidation by mixture $NO/O_2$. These characteristics are superior to those typical of Pt-$MnO_x$-$Al_2O_3$ and Pd-$MnO_x$-$Al_2O_3$ catalysts containing 0.70 g/L of Pt or Pd.

The catalytic activity in light hydrocarbon oxidation is shown to correlate with the RedOx properties of PdPt-$MnO_x$-$Al_2O_3$ catalysts and Pt-Pd particle size. The non-additive increase in the catalytic activity of the bimetallic catalyst is suggested to connect with a formation of PdO-$PtO_x$ clusters on the surface of $Mn_3O_4$ and PtPd clusters. The improvement of catalytic performance of the aged catalysts in the reactions of hydrocarbon oxidation and NO reduction can be related to coarsening of the clusters to nanoscale PdO-$PtO_x$ particles, which are characterized by the reversible RedOx transformations of Pd(Pt)-PdO($PtO_x$) - Pd(Pt) during TPR and catalytic experiments.

Prospects of the application of the Pt-Pd-$MnO_x$-$Al_2O_3$ monolithic catalyst in the diesel exhaust post-treatment systems will be discussed.

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# Catalytic laboratory reactors: Solutions from Parr Instruments

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During more than century existence Parr Instruments Company specializes in high pressure high temperature reactors manufacturing. After patenting of well-known Parr oxygen calorimeter bomb[1], the company has produced thousands of different reactor systems, which are successfully used in many thermochemical and catalytic laboratories worldwide. At present time the company can propose many different reactor types from various standard model lines[2] allowing high flexibilities in final reactor composition. To be even more flexible Parr can manufacture custom setups composed of several reactors or including different custom instruments for reaction study and control.

A typical tabletop stirred reactor consist of reaction vessel itself, temperature control system, stirring system, pressure control system, safety system and various components for reagents addition and sampling. Reaction vessels available in different sizes (25 ml to several liters) and have two designs – fixed-head and moving head. Fixed-head means permanent fixation of the reactor head on the stand. As reactor head contains all connections and instruments this is very useful to let everything undisturbed at time of opening. Inside access in this case is done via removing split ring and lowering the cylinder. The second type – movable vessel, allows removing whole vessel away from the stand, which is helpful if there are not a lot of connections on reactor head.

Vessels can be made from different materials. While 316L (medical stainless steel) is most common, some situations, i.e. highly aggressive medias, could lead to other alloys – 600, 20, C-276, G45 etc. and pure - metals nickel, titanium, tantalum. As the corrosion properties of the planned reaction system can be predicted, it is really important to know the process to make wise material choice. In some cases, glass or PTFE liners can be used to protect the inside of the reactor from corrosive species. The speed of corrosion increase exponentially with the temperature and this is a main reason to be concerned, if corrosive species are present in the reactor.

Stirring is done via magnetic coupling and electric drive on the stand. The power of coupling and drive can vary adopting mixing of viscous fluids. Different types of impellers ensure uniform mixing and could allow gas delivery through impeller vanes. The temperature control system is a heater with two thermocouples – one for the heater and one inside the reactor. The additional chiller with inner coil can be used for fast cooling. Pressure can be read from the gage or from dedicated electronic detector on the controller. The last allows pressure control, i.e. with solenoid valve. Safety systems include Inconel rupture disc protection from overpressure and independent overheating control with heater power off and cooling coil opening. Generally, pressure rating of reactors varies from 200 bar to 350 bar. Temperature raiting: 350 °C with PTFE seals and °500 C with flexible graphite seals. Custom solution can withstand higher pressures and temperatures.

There are a lot of possible systems for reagents input and sampling under pressure, including manual and automatic gas & liquid sampling, solids addition under inert gas etc. Catalysts can be loaded in baskets or placed in the breakable glass vials, which allow start the reaction at preselected pressure.

Systems could include several reactors of different forms, i.e. tubular reactors, separators, stirred reactors, various instruments and controls, i.e. probes, valves, pumps, filters, safety elements etc. Everything is mounted on one floor stand with wheels, and controlled automatically via computer based software. Reactors systems are built on demand using all available proven technologies.

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# The production of refining catalysts of PJSC, Gazprom Neft

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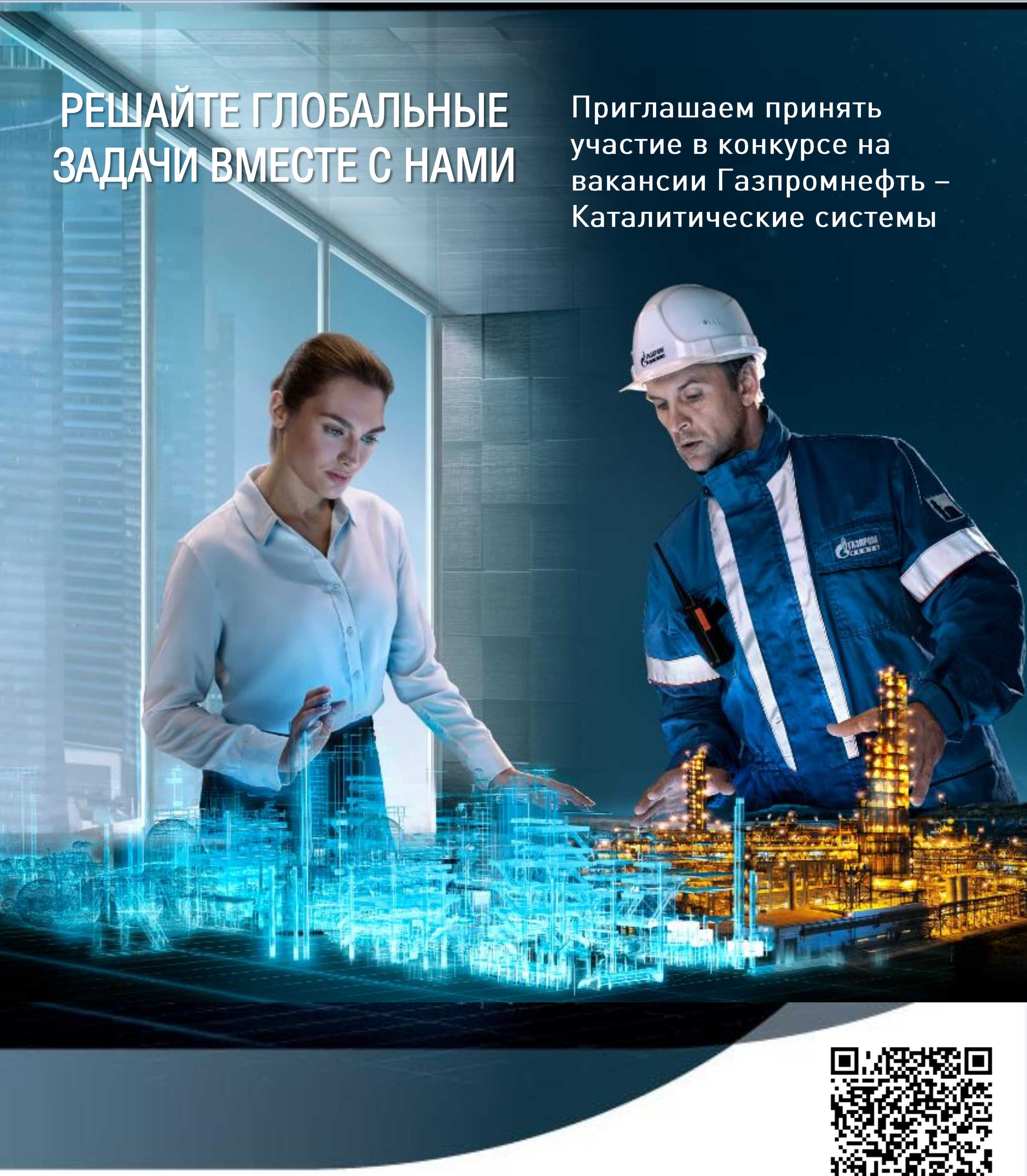
Currently, PJSC Gazprom Neft is implementing more than 30 R&D projects in the field of oil refining, which allows the Company to hold leading positions in the Russian market. One of the priorities of PJSC Gazprom Neft is the development of new high-tech areas, among which a special place is given to the project of construction of a new refining catalyst plant in Omsk with a capacity of 21 thousand tons per year. In 2015, the Ministry of Energy of the Russian Federation assigned the project a national status. In 2016, a subsidiary of LLC Gazpromneft-Catalytic Systems was established to manage the catalytic business of the Company. The construction will be completed and production will be put into operation in mid-2020. As a result of the project will be established a modern production of refining catalysts: with production of the cracking catalysts – 15,000 tons, production of the hydrotreating catalysts – 4,000 tons, production of the hydrocracking catalysts – 2,000 tons. The development of innovative technologies of catalysts production for catalytic cracking and hydroprocessing is carried out in close cooperation with the leading Russian scientific organizations – the Institute of Hydrocarbons Processing SB RAS and Boreskov Institute of Catalysis SB RAS.

Furthermore, right now, within the project, has been opened a unique engineering center for catalyst testing, equipped with the only pilot catalytic cracking plant in Russia. In the near future, the engineering center will additionally be equipped with modern equipment for testing, research and production of experimental batches of catalysts for secondary processes of oil refining.

LLC Gazprom Neft-Catalytic Systems will be able to offer not only effective catalysts to the Russian refineries, but also a full package of services: simulations of catalyst operation, pilot tests, calculations of catalyst loading, monitoring of unit operation, sample analysis, development of recommendations for process optimization, etc.

The implementation of such a large-scale project is impossible without the involvement of highly qualified specialists, as well as the establishing of a system of targeted continuous training and staff development. In 2019-2020 LLC Gazpromneft-Catalytic Systems will create more than 120 new workplaces in the field of development of new types of catalysts, the production of catalysts, as well as service support for consumers of catalysts and services.

In order to ensure effective commissioning of the catalysts production plant and timely training of personnel, LLC Gazpromneft–Catalytic Systems begins to form a candidates pool and is ready to consider for employment a graduates of specialized universities of Omsk, Novosibirsk, Tomsk and other Russian cities.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Мы стараемся поддерживать максимально полную линейку оборудования с метрологической поддержкой для контроля качества нефтепродуктов, начиная от пробоотборников для резервуаров хранения и транспортировки и заканчивая мультипараметрическими мобильными экспресс-методами анализа основных параметров на конечной стадии потребления. Для научных и исследовательских лабораторий мы предлагаем более широкий спектр оборудования, включая:

- аналитические весы, тензиометры, анализаторы краевого угла
- муфельные печи, термошкафы, термостаты, инкубаторы,
- сушильные шкафы, испытательные камеры, центрифуги,
- стеклянные реакторы и реакторные установки,
- проточные и стационарные реакторы высокого давления,
- высокотемпературные коррозионностойкие реакторные системы,
- анализаторы содержания отдельных компонент в сложных смесях,
- анализаторы содержания серы и других элементов в жидкостях,
- анализаторы размеров частиц и дзета-потенциала,
- счетчики и датчики частиц в топливах, воздухе, газах и воде,
- системы фракционирования (FFF), ВЭЖХ и ВЭЖЖХ,
- селективные детекторы и системы преконцентрирования для ГХ
- анализаторы молекулярной массы полимеров и других макромолекул
- анализаторы динамической и статической сорбции паров,
- бомбовые, реакционные и адиабатические калориметры,
- специализированные анализаторы для контроля качества масел, смазок и битумов,
- титраторы, плотномеры, вискозиметры, рефрактометры,
- трибомашины и встраиваемые датчики удаленного контроля состояния смазки,
- индикаторные трубки и другие анализаторы микропримесей в газах,
- потенциостаты, гальваностаты, ячейки и другое электрохимическое оборудование,
- общелабораторное аналитическое оборудование и мебель.

За долгие годы существования в компании **SocTrade™** сложился коллектив специалистов, который способен решить практически любую задачу, относящуюся к подбору оборудования, созданию систем, организации контроля или к разработке аналитических и контрольных методик. Мы не только поставляем оборудование, но и оказываем техническую и методическую поддержку, обеспечиваем сервис, производим гарантийное и послегарантийное обслуживание, а также помогаем в постановке методик анализа и решении проблем аттестации и поверки лабораторного оборудования.

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# SECTION 1

## CATALYST PREPARATION

# Bismuth silicates prepared via mechanochemical activation for photocatalytic applications

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Bismuth silicates are a family of compounds which is classified as complex oxide systems. Bismuth metasilicate $Bi_2SiO_5$ is a substance of Aurivillius family with perovskite-type structure. At the same time, the structure of bismuth orthosilicate $Bi_4Si_3O_{12}$ is transitional from perovskite-type to framework, while the one of sillenite $Bi_{12}SiO_{20}$ is purely a framework similar to $\gamma$-$Bi_2O_3$. These structural differences provide a sufficiently broad range of peculiar physical and chemical properties. For example, $Bi_4Si_3O_{12}$ can be used as potential scintillator material [1] due to lower production cost than that of bismuth orthogermanate $Bi_4Ge_3O_{12}$, while having otherwise similar parameters. Up to the current date, there are several new reports, which also indicate on high potential of different bismuth silicate compositions in photocatalytic applications [2, 3].

In this work, environmentally friendly mechanochemical activation was applied, available to carry out the process with great speed in the absence of any solvent. With this method of synthesis, the influence of molar ratio of initial reagents on phase composition and properties of prepared samples was investigated.

For the first time, bismuth silicates were obtained via mechanochemical activation followed by calcination. Bismuth oxide $Bi_2O_3$ and hydrous silica $SiO_2 \cdot nH_2O$ were used as precursors. The stoichiometric mixtures with different composition were activated in a high-power planetary ball mill AGO-2 for 10 min [4]. The mixtures activated for 10 min were calcined at different temperatures for 2 h, with calcination temperatures being chosen with accordance to the data of TG-DSC.

Combined analysis of XRD and TG-DSC data shows that the initial molar ratio of $Bi_2O_3:SiO_2 = 6:1$ ultimately leads to the formation of $\gamma$-$Bi_{12}SiO_{20}$, which decomposes at 875 °C. The formation of $Bi_2SiO_5$ phase (primary) and $\gamma$-$Bi_{12}SiO_{20}$ (impurity) is indicated in the sample with the molar ratio of $Bi_2O_3:SiO_2 = 1:1$ in the course of calcination of mixtures activated at 500°C. At 600°C metastable $Bi_2SiO_5$ phase is partially transformed to $Bi_4Si_3O_{12}$. With the molar ratio of $Bi_2O_3:SiO_2 = 2:3$, at 500 °C two modifications of $Bi_2SiO_5$ phase are formed at the same time as $Bi_4Si_3O_{12}$. At 600 °C bismuth metasilicate phase completely transforms to $Bi_4Si_3O_{12}$ phase with the formation of $\gamma$-$Bi_{12}SiO_{20}$ phase as impurity.

Photoluminescence effect was detected for all samples containing $Bi_4Si_3O_{12}$ phase, with the excitation peak at 250 nm. Other materials do not possess photoluminescence effect at all. UV-VIS diffuse reflectance spectroscopy data shows that prepared bismuth silicates absorb visible light and with accordance to XRD data possess different phase composition.

As shown above, mechanochemical activation for 10 min does not allow to synthesize single phase samples with molar ratio of $Bi_2O_3:SiO_2 = 1:1$ and 2:3. Apart from expected stoichiometric phases, other phases of bismuth silicates are also detected. Multiphase composition can possibly be attributed to complex mechanisms of nuclei formation in the course of solid state reactions.

A photocatalytic study of all prepared materials in the reaction of Rhodamine B photodecolorization is expected. Additionally, a series of bismuth silicates prepared via conventional hydrothermal method will be discussed in the study, investigated with the methods described above to provide comparison.

*This research was supported by "The Tomsk State University competitiveness improvement programme".*

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# In-situ SAXS study of the $TiO_2$ aggregation mechanisms: Influence of the $C_1$-$C_4$ alcohols and water

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Titanium dioxide has a lot of application in the paint production, photocatalysis, catalysis and others areas of industry [1]. The advanced materials from titanium dioxide with required properties are often size dependent and it is essential to be able to control the particle size, shape, and size distribution. Respectively this needs a detailed understanding and managing of the mechanisms of growth of titanium nanoparticles at their production. One of the popular ways of nano-sized $TiO_2$ preparation it is sol-gel synthesis from titanium alkoxides [1]. There is a lot information about mechanism of $TiO_2$ aggregation in the water media or media enriched by water [1, 2]. Nevertheless, hydrolysis of Ti alkoxides in alcohol media has not studied enough. Whereas changing of water phase on the organic phase can give some new possibilities in managing of $TiO_2$ nanoparticles aggregation processes.

In our work we studied hydrolysis of titanium butoxide in the alcohols media with small quantity of water and HCl as acid catalyst. The molar ratio titanium butoxide/water has been varied from 1:2 to 1:32. In the case of alcohol media has been used methanol, ethanol, propanol, butanol and their mixtures. For determination $TiO_2$ nanoparticles sizes in sols it has been used SAXS. According SAXS data the $TiO_2$ nanoparticles in sols have Gauss-like chains shape and radii gyration ($R_G$) values in the range from 1.5 to 7.0 nm depending from the time of sols aging. It has been shown that typical mechanism of $TiO_2$ particle aggregation in $C_3$-$C_4$ and higher alcohols is realized in coalescence regime. In the case of using methanol or ethanol the aggregation mechanism is changing on the faster process Ostwald ripening. Using different mixtures ($C_1$, $C_2$/$C_3$, $C_4$) is allowed to tuned needed mechanisms of aggregation processes. Moreover, changing of molar ratio titanium butoxide/water in reaction mixture also influence on the type of mechanism aggregation. At increasing water loading starts to realize mechanism of Ostwald ripening.

*This work was conducted within the framework of budget project No. 0303-2016-0002 for Boreskov Institute of Catalysis*

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# Synthesis of bifunctional Ag–Pd@UiO-66 catalysts with different methods

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Catalytic conversion of biomass and products of its processing attracts growing attention due to limited traditional carbon sources such as fossil hydrocarbons. One of the main challenges of biomass valorization is the development of multifunctional catalysts, e.g., heterogeneous systems containing active sites with different nature for cascade-type reactions.

The aim of the present investigation is to develop the bifunctional catalyst with redox active species combined with Lewis acid active sites. This idea can be realized by application of metal–organic framework UiO-66 as a support-cocatalyst for Ag–Pd nanoparticles due to high concentration of Lewis acid active sites, high thermal, chemical and aqueous stability, large specific surface area and high pore volume [1]. UiO-66 is a porous zirconium terephthalate consisting of $Zr_6O_4(OH)_4$ octahedrons connected with terephthalic acid that forms a 3D porous network. A combination of Ag–Pd bimetallic nanoparticles as redox species and Lewis acids sites of UiO-66 has a great potential to produce an active catalyst for cascade-type reactions.

The most common approaches to immobilize metal nanoparticles in MOF are “ship in a bottle”, “bottle around a ship” and solution impregnation methods. All techniques have some drawbacks, including possibility of collapse of the MOF structure, pore space blocking or formation of large metal particles on the external surface of MOF particles.

Nowadays there are a few reports on immobilization of silver/palladium nanoparticles in MOFs. Metal nanoparticles prepared via “double solvent” approach had very small particle size [2]. Immobilization of silver nanoparticles in UiO-66 was realized via solution infiltration method [3], however, the final particle sizes were about 7-10 nm, which was much higher in comparison with pore sizes of UiO-66 (0.9 and 1.1 nm).

Immobilization of Ag–Pd nanoparticles was performed by different techniques, such as wetness impregnation of water or acetonitrile silver nitrate solutions and palladium nitrate/acetylacetonate solution, double solvent approach and self-developed wetness impregnation method with one-pot chemical reduction technique. The effect of impregnation technique on the catalyst structure and activity was tested by XRD, low-temperature nitrogen adsorption, DRS UV-vis and TEM methods. Catalytic properties were studied in aerobic oxidation of propylene glycol into lactic acid.

Bimetallic nanoparticles were successfully immobilized inside the pores of UiO-66 by “double solvent” and wetness impregnation methods with one-pot chemical reduction technique. Formation of small metal nanoparticles (<3 nm) was confirmed by XRD and TEM methods. Low-temperature nitrogen adsorption analysis showed that the large part of UiO-66 pore volume was still available for substrate. The use of acetonitrile solution of palladium acetylacetonate and silver nitrate instead of silver and palladium nitrates mainly led to formation of Ag and Pd monometallic particles, which was confirmed by DRS UV-vis and XRD methods. The influence of Ag/Pd ratio and reduction conditions will also be discussed.

*This work was supported by Tomsk State University competitiveness improvement program.*

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# Monolithic silica gels prepared by sol-gel method

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Monolithic materials are characterized by a continuous three-dimensional structure which provides access to the surface for a variety of applications. Monoliths are used in different processes, including the emission control of industrial and automobile gases, catalysis, and high-performance liquid chromatography [1, 2].

These materials should possess a selection of characteristics, i.e. mechanical strength, permeability, meso- and macropore ratio, heat and mass transfer efficiency, specific surface area, etc. It is possible to produce materials with necessary properties via careful control of conditions and chemical composition. Organic polymers and silica monoliths offer the possibility of surface modification. However, silica monolith is more resistant to a wider range of solvents, and possesses higher thermal and mechanical stability. The homogeneity of both macroporous space and skeleton thickness of monolithic silica, offering the opportunity to make efficient and selective catalysts with narrow residence time distributions, is an advantage over packed beds.

Porous $SiO_2$ monoliths with different compositions were prepared by sol-gel method with the use of TEOS as a $SiO_2$ precursor, CTAB and/or PEG as porogens [3, 4]. The monoliths were characterized using BET, SEM, and water permeability using Darcy's law. The porosity was determined by weighing the dried and water-saturated monoliths.

Silica monoliths with two types of structure were prepared with a careful control of chemical composition and concentration range of porogen/$SiO_2$. Silica monoliths of type A1 were prepared in the concentration range of porogen/$SiO_2$ from 0.35 to 0.56 and were found to have bicontinuous structure. These silica monoliths A1 are bimodal having both interconnected flow-through pores and those located in silica skeleton. In this range, as the polymer concentration increases, the size of macropores and the thickness of skeleton decrease from 41 and 24 μm to 7 and 3 μm, respectively. This leads to a decrease in strength of the materials from 2 to 1.2 MPa. The presence of large macropores promotes high values of permeability of monoliths ($3.5 \cdot 10^{-12}$ m$^2$).

The second type of the silica monoliths (A2) was prepared in the concentration range of porogen/$SiO_2$ from 0.24 to 0.54. These monoliths had the globular structure with interconnected macropores in the concentration range of porogen/$SiO_2$ from 0.24 to 0.42. Monoliths of the A2 type possessed high porosity and low skeleton strength which resulted in high permeability (up to 7·10–12 m2). Silica A2 with more strength was formed due to an increased amount of porogen. These monoliths had mesoporous structure and were proven to have low permeability ($8 \cdot 10^{-16}$ m$^2$). All monoliths had high porosity (85-92 %) and specific surface area (220-350 m$^2$/g).

Monolithic $SiO_2$ having bicontinuous structures were discussed in this thesis. The monoliths of A2 type are weaker than the ones of A1 type which may lead to destruction of their skeleton. Low strength of A2 type makes it possible to use these only in processes with low resistance of the medium. Properties of A1 silica monoliths allow to consider it as a catalyst support for flow-through reactor in liquid-solid reactions.

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# Synthesis of mesoporous silica MCM-41 from sodium silicate: the effect of CTAB:Si ratio

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The template synthesis is interesting process among methods of synthesis porous silica gels. Pore size can be controlled by adding the surfactant that leads to ordered silica assembling. Silica with structure of MCM-41 has regular porous structure, which is assembled by lingering open cylindrical channels with diameter of 2-4 nm. It has high values of specific surface area (over 1000 $m^2/g$), high thermal stability and wide range of potential applications in sorption, as support for heterogeneous catalysts. However, the application of MCM-41 is limited by high cost of material because expensive tetraethoxyortosilane (TEOS) and cetyltrimethylammonium bromide (CTAB) is used generally as precursor of silica and surfactant-temple, respectively. Sodium silicate ($Na_2O\cdot nSiO_2$) is another possible cheaper precursor of silica, however, template synthesis of mesoporous silicates from sodium silicates is not enough studied.

The present work is devoted to the study the dependence of the structure and properties of the material MCM-41, synthesized from sodium silicate, from the conditions of synthesis. Special attention is given to effect of CTAB/Si ration on structure of MCM-41 with low CTAB concentration (CTAB/Si<0.4). The MCM-41 was synthesized with composition of $525(H_2O):X(CTAB):1(SiO_2)$, X = 0.025–0.4. MCM-41 was obtained in water at pH ≈12 without catalyst by mixing of CTAB solution and sodium silicate solution with following by hydrothermal treatment at 110 °C during 24 h. Then, materials were washed by distilled water and calcined at 540 °C during 10 h. The structure of MCM-41 was studied by low-temperature $N_2$ adsorption using 3Flex analyzer (Micromeritics, US). The specific surface area (SBET) of the MCM-41 calculated from the absorption branch of isotherm in the range of relative pressures from 0.02 to 0.20. Pore size distributions were calculated with using of BJH method, Horvath-Kawazoe and DFT.

It was shown that silica with structure of MCM-41 can be obtained from sodium silicate. The adsorption-desorption isotherms for prepared samples have a high adsorption step at relative pressures of 0.2-0.35 that confirm the formation of silicate with structure of MCM-41 with narrow pore size distribution. The MCM-41, synthesized with ration CTAB/Si = 0.05 and 0.075, are characterized by narrowest pore size distribution from 3.2 to 3.9 nm (width at half-height pore size distribution W1/2=0.19 nm). With growth of ratio CTAB:Si from 0.025 to 0.4 the specific surface area increase from 1120 to 1384 $m^2/g$, that is attributed with pore size decrease.

Thus, it was shown that synthesis of MCM-41 with well-ordered structure may be realized with using of sodium silicate as silica precursor and small amount of CTAB. Growth of CTAB amount above CTAB/Si>0.1 leads to increased SBET but the ration CTAB/Si=0.05 is optimal for synthesis of MCM-41 with narrowest pore size distribution.

# Synthesis and properties of complex Manganese-Aluminum-Phosphates $Mn_{0,5(1+x)}Al_xTi_{2-x}(PO_4)_3$ in ethanol conversion

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Complex phosphates with the NASICON structure have attracted the attention of researchers due to their unique set of properties determined by their structure and composition. These systems have high ionic conductivity, low thermal expansion coefficient, and low thermal conductivity. Their high chemical, radiation, and thermal stability, and high hardness are also significant. NASICON phosphates have a catalytic activity in reactions of selective dehydration of lower aliphatic alcohols, selective catalytic oxidation of alkanes, alkenes and alcohols [1, 2]. Due to the wide isomorphism in all crystallographic positions of NZP-phosphates, the properties of the final product can be varied, which makes it possible to synthesize the catalyst for a specific chemical process [3, 4].

In this study, we have researched correlation between phase composition of materials and their physical and chemical properties that allow to obtain high resistant materials with the desired properties such as high thermal phase stability, specific surface area and catalytic activity and selectivity in the long term.

The catalytic activity of the samples $Mn_{0,5}Ti_2(PO_4)_3$, $Mn_{0,7}Al_{0,4}Ti_{1,6}(PO_4)_3$ has been studied in the model ethanol conversion reaction in flowing unit in the 200-400°C temperature range with gas chromatographic analysis of products.

The results showed that on both samples ethanol was transformed to ethylene, diethyl ether and acetaldehyde. The sample composition significantly influences the selectivity of the alcohol conversion: the main reaction on $Mn_{0,5}Ti_2(PO_4)_3$ is dehydrogenation to acetaldehyde. The predominance reaction on the same systems doped with aluminum is dehydration to diethyl ether. The difference in the catalytic activity of the samples is due to the change of the active site (change in the activation energy of the reaction) caused by the distortion of the $PO_4$-tetrahedra of the NZP structure upon the addition of aluminum

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# A new low-temperature route to produce perovskite-type nanoparticles

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In recent years, in connection with the increasing environmental pollution, several studies have carried out investigations of a new group of compounds. In the current work perovskite-type $MTiO_3$ (M= Cd, Co, Cu, Ni)/$TiO_2$ nanoparticles have been synthesized through the thermal decomposition of organometallic complexes, based on pyrocatechol, titanium butoxide (IV) and different d- metals. The preparation process is represented in scheme:

$$Ti(OC_4H_9)_4 + M(NO_3)_2 + H_2L \xrightarrow{40\ ^\circ C\ (3.5\ h) + 25\ ^\circ C\ (6\ h)} Ti(L)_2M \xrightarrow{\text{calcination: } 550\ ^\circ C\ (3.5\ h)} MTiO_3$$

where $Ti(OC_4H_9)_4$ – titanium butoxide (IV), $H_2L$ – pyrocatechol, $Ti(L)_2M$ – organometallic complexes, $M(NO_3)_2$ – mono-, tetra- or hexahydrate nitrate of the corresponding metal.

All reactions were carried out under an inert atmosphere of dry argon using standard Schlenk techniques. Solvents used in reactions were dried by standard methods and degassed prior to use.

Synthesizing perovskite-type titanates were carried out at different period of time and temperature. The most optimal situation was recognised at 550 °C for 3,5 hours. After calcination, the obtained nanoparticles are highly crystalline and monodisperse in size. The result shows this type of experiment can help to obtain $MTiO_3$ nanoparticle at less temperature, than in previous work we reported [1].

Characterization of the complexes and nanoparticles has been done by X-ray diffraction (XRD), FT-IR spectroscopy, UV-Vis spectroscopy, Field emission scanning electron microscope (FESEM) image and $N_2$-adsorption (BET analysis). Almost all obtained nanoparticles exhibit the characteristic diffraction peak of $TiO_2$ anatase phase at $2\theta = 25{,}319$ °.

According to the synthesis, while organometallic complexes as a precursor was being reacted with the metal, the energy band gap has been decreased markedly. The relationship between energy band gap and crystallite sizes is inverse, meaning that by decreasing crystallite sizes, more UV light is absorbed.

Finally, pyrocatechol was the target as the phenolic harmful compound, to be degraded by the obtained nanoparticles. The photocatalytic degradation was carried out under the irradiation UV light. The kinetics of pyrocatechol degradation is described in accordance with the first-order reaction equation.

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# Synthesis and study of macroporous tin (IV) oxide as an electrocatalyst support

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Due to its physicochemical, optical and electric properties, tin (IV) oxide is widely used in lithium-ion batteries, gas sensors, sensitized solar cells and as a support for electrocatalysts [1]. One of the most perspective $SnO_2$ application is to use it as a support for Pt electrocatalysts in fuel cells. Pt catalysts based on tin (IV) oxide have a higher corrosion resistance compared to that of conventional Pt catalysts based on carbon black [2]. It results in increasing durability of the electrocatalysts and thus in increasing fuel cell lifetime. In this paper, we investigate possibility of macroporous tin (IV) oxide application as a support for Pt electrocatalysts in fuel cell.

Polystyrene (PS) microspheres with average diameter of ~ 250 nm were used as a hard template for the synthesis of macroporous tin dioxides. They were prepared using 4,4′-azobis(4-cyanovaleric acid) as an initiator for styrene polymerization in accordance with the following work [3]. The first series of tin (IV) oxides was synthesized by aging of soles from tin (IV) chloride in the presence of PS microspheres suspension in water-ethanol solution. The PS was removed from $SnO_2$ samples by annealing at 450°C in $O_2$. The final powders were yellow. The second series of tin dioxide was synthesized from tin (II) oxalate. At first stage, tin (II) chloride was precipitated by $(NH_4)_2C_2O_4$ in the presence of PS suspension while stirring. Then PS was extracted from $SnC_2O_4$ by toluene. The samples of $SnC_2O_4$ were heat treated at 400°C to provide thermal decomposition. The final $SnO_2$ powders were brown.

Physicochemical characterization of $SnO_2$ samples was carried out using low-temperature $N_2$ adsorption (77 K), Hg porosimetry, the scanning and the transmission electron microscopies, X-Ray diffraction, X-ray photoelectron spectroscopy and CHNS analysis. The corrosion stability of $SnO_2$ samples was studied by using accelerated “Start/Stop cycling” protocol in 1 – 1.5 V RHE of the potential range in 0.1 M $HClO_4$ electrolyte. The curves of cyclic voltammograms were recorded in the range 0.05 - 1.2 V RHE with a sweep rate of 0.05 V/s before the "Start/Stop cycling" protocol and every 2000 cycles. Electric conductivity was studied by the impedance spectroscopy in $10^{-1}$ - $10^{5}$ Hz of the frequency range at the room temperature and pressure of 1.3 MPa using home - made cell.

The final tin (IV) oxide samples had a bimodal pore distribution and spherical macropores with an average diameter of 110 - 180 nm. It had been found that corrosion resistance and conductivity of the samples prepared from $SnCl_4$ and $SnC_2O_4$ increased with increasing of the mass ratio of PS `precursor salt. It could be accounted for by particle sintering while composite calcination. At the same time, increase of sols aging time also led to the increase of corrosion resistance and conductivity. It can be resulted from increasing crystallinity of tin (IV) oxide samples. The corrosion resistance of $SnO_2$ samples was comparable with that of commercial carbon black Vulcan XC-72.

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# Synthesis and investigation of monolithic catalysts based on transition metal oxides for catalytic air heaters

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Catalytic air heaters are the autonomous heat sources serving as an alternative to centralized heat supply; they can significantly reduce the cost of thermal energy transportation, distribution and consumption. The operation of catalytic heat sources is based on utilization of energy released by the exothermic reaction of complete oxidation of hydrocarbon fuels on a catalyst.

Oxide catalysts based on transition metals (Mn, Fe, Ni, Co, Cu) that are deposited on a structured support are the efficient catalysts for complete oxidation of hydrocarbons. Such catalysts combine the high potential catalytic activity of transition metals and the advantages of structured supports. The studies aimed to develop environmentally friendly monolithic oxide catalysts with a high catalytic activity are topical for solving the problems of safe combustion of fuels.

**The goal of the work:** to investigate the formation features of oxides in single- and two-component monolithic catalysts for complete oxidation of hydrocarbons.

To accomplish the goal, **the following tasks were set in the work:**

1. Synthesis of single- and two-component monolithic catalysts based on oxides of transition metals (Mn, Fe, Co, Cu, Ni).
2. Investigation of textural, morphological and structural properties of the synthesized catalysts by different physicochemical methods: BET, XRD, TEM, SEM, TPR $H_2$, UV-vis spectroscopy, and differential dissolution.
3. Elucidation of relations between features of the active component, its location in the support matrix, and catalytic activity in complete oxidation of butane.

In the single-component catalysts with Mn, Fe, Co, Ni or Cu, the active component is represented by well crystallized oxide phases consisting of the aggregates of particles having the size of 100-150 nm and different interaction strength with the support.

A simultaneous introduction of Mn and transition metal oxides (Fe-Mn, Ni-Mn, Co-Mn, Cu-Mn) changes the phase composition and reducibility with hydrogen, decreases the size of oxide particle aggregates to 20-100 nm, and enriches surface layers of the support with manganese cations (from 24 % in the single-component Mn catalyst to 48 – 84 % in two-component systems depending on the catalyst composition). HRTEM, TPR $H_2$ and UV-vis spectroscopy studies revealed that the active components are represented by a mixture of phases of simple oxides and mixed one-cation and multi-cation oxides. The introduction of the second component in the Mn catalyst non-additively increases the activity in comparison with the single-component catalysts and their mechanical mixtures. The synergetic effect is caused by a set of factors, in particular, the formation of the interaction phases between oxides, a decrease in the size of active component aggregates, and an increase in the amount of Mn cations in subsurface layers of the support in one-cation and multi-cation oxides.

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# Specific aspects of Mn, La-Mn, Ce-Mn oxides formation in monolithic catalysts under SCS method conditions

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The properties of supported catalysts are determined not only by the nature of active component, of strategic importance is also the choice of the support type and synthesis method. Structured supports, due to their unique properties, are more preferable for application in the processes with high linear rates of gas flows than granular supports. Selection of a method for the synthesis of catalysts on structured supports is limited by adhesion and textural properties of the supports. Some works demonstrated that the solution combustion synthesis (SCS) is a promising method for the production of structured catalysts; however, the literature does not provide systematic data about the effect exerted by this method on the structure of support and on the state of active component and its location in the support matrix. The SCS method is a variant of self-propagating high-temperature synthesis (SHS) and is based on the exothermic reaction between active component precursors and a fuel additive (urea, glycine, hydrazine, citric acid, etc.), which proceeds directly on the support surface at relatively low temperatures.

**The goal of the work:** to elucidate the formation features of oxides in single- and two-component monolithic catalysts based on Mn, La and Ce and their location in the ceramic support matrix during the synthesis by SCS and impregnation methods.

To accomplish the goal, the following tasks were set in the work:

1. Synthesis of single- and two-component monolithic catalysts based on Mn and rare-earth element (La and Ce) oxides by SCS and impregnation methods.
2. Elucidation of the effect exerted by the synthesis method on physicochemical properties of the catalysts and their activity in complete oxidation of butane.

Investigation of the Mn, La-Mn and Ce-Mn catalysts synthesized by impregnation and SCS methods demonstrated that specific surface area, reducibility with hydrogen, particle size, stabilization of the active component and its localization depend on the synthesis method.

The application of SCS method increases the fraction of mesopores and the specific surface area owing to spontaneous pore formation upon pulsed release of the gaseous products of the combustion reaction.

The TPR $H_2$ study showed that under the SCS conditions more reduced forms of Mn oxide are formed as compared to the impregnation method, the fraction of Mn (+3, +4) oxides decreases, and the fraction of Mn (+2) oxides increases.

The application of SCS method and an increase in the amount of fuel additive decreased the size of aggregated particles of the active component (8-30 nm for SCS, and 15-100 nm for impregnation method) and enriched subsurface layers of the support with manganese cations (65- 94% for SCS, and no more than 55% for impregnation method), thus making the catalytic sites accessible to reactants and strongly enhancing the catalytic activity in complete oxidation of butane as compared to the impregnation method.

The active component particles formed under the SCS conditions are more strongly confined in subsurface layers of the support and are less prone to sintering, thus providing a more stable long-term operation of the catalysts in comparison with the impregnated catalysts.

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# Effect of preparation method on physicochemical and functional properties of Ni/$CeO_2$-catalysts

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Ni-Ce-O materials are widely applied for various catalytic reactions such as total oxidation of CO and volatile organic compounds, the reforming of hydrocarbon fuels or the hydrogenation reactions [1-3]. Their unique catalyst performance is connected with the ability of Ni to break effectively C–C and C–H bonds as well as the contribution of ceria to the activation of the O-H bond. It has been shown that a strong metal-support interaction between nickel and ceria facilitates oxygen transfer and suppresses deactivation through sintering and coke formation. The preparation mode is one of the key factors the variation of which provides the regulation of strength of metal-support interaction for efficient control of the structural, electron and red-ox characteristics of the active component and, consequently, functional catalyst properties. So, in this work, the effect of preparation method on physicochemical and functional properties of Ni/$CeO_2$-catalysts was studied. Our strategy was to achieve high catalytic activity and material stability against deactivation by the use of $Ce_{1-x}Ni_xO_y$ mixed oxides as precursors of Ni/$CeO_2$ catalysts.

The Ni/$CeO_2$-catalysts with different Ni content (0-15 wt.%) were prepared by the incipient wetness impregnation (I-series) and polymerizable complex (P-series) methods. To establish the composition-structure-properties correlation, the catalysts were characterized by a group of methods (TG-DTA, BET, XRD, HRTEM-EDX and $H_2$-TPR) and tested in the reaction of autothermal reforming of ethanol at atmospheric pressure, temperature 200-700°C, a flow rate of 320 mL/min and the molar ratio between reagents $C_2H_5OH : H_2O : O_2 : He = 1 : 3 : 0.4 : 0.7$.

The peculiarity of the Ni/$CeO_2$ catalyst genesis was studied by thermal analysis. It was shown that by contrast to the multi-stage degradation of the polymer precursor of Ni/$CeO_2$ (P) that proceeds with exo-effects, the decomposition of supported Ni nitrate of Ni/$CeO_2$ (I) is accompanied by endo-effects. The calcination at 500°C leads to the formation of mesoporous materials. It was established that the textural characteristics, phase composition and reducibility of Ni/$CeO_2$-catalysts were affected by the Ni content and preparation method. In contrast to I-series, P-series of catalysts were characterized by higher $S_{BET}$ and $V_{pore}$, values of which grew with an increase of the Ni content. The XRD data show that for Ni/$CeO_2$ (I) the main phases are $CeO_2$ and NiO, while for Ni/$CeO_2$ (P) only a ceria-based solid solution. For I-series of samples the crystallite size of $CeO_2$ is equal to 11 nm and does not change with an increase of the Ni content. On the contrary, for P-series the crystallite size of $CeO_2$ decreases from 11 to 5.5 nm at an increase of the Ni content from 0 to 15 wt.%. With a growth of the Ni content, the increase of the material reducibility is observed.

The functional properties of Ni/$CeO_2$-catalysts were comparatively studied in the autothermal reforming of ethanol and effects of Ni content and preparation method were elucidated. The behavior of the catalytic activity and the coking mode are discussed in correlation with physicochemical properties of Ni/$CeO_2$. The optimal catalyst composition and preparation mode were selected.

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# Synthesis of hybrid materials N-hydroxyphthalimide@Co-MOF/$SiO_2$ as catalysts for oxidation of hydrocarbons

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Selective catalytic oxidation of hydrocarbons into value-added derivatives with dioxygen is a fundamental transformation in organic chemistry. However, still the activation of C–H bond and prevention of overoxidation is a challenging task. Generally, industrial catalysts employed in the liquid-phase oxidation of alkanes and cycloalkanes are homogeneous materials based on transition metal salts. Such processes produce a large amount of environmentally undesirable wastes and require complicated procedures for the catalyst separation and product purification. N-hydroxyphtalimide (NHPI) is known as a valuable catalyst for aerobic oxidation of various organic compounds [1]. Its activity is related to the formation of phthalimide N-oxyl (PINO) radicals that abstract hydrogen from the substrate. The PINO formation is usually facilitated by the additives of transition metals [2] such as, for example, Co(II) salts. In the present work we managed to synthesize heterogeneous catalyst that contains both Co(II) and NHPI through immobilization of NHPI into the pores of Co-based silica-supported metal-organic framework (MOF).

Two kinds of silica surface modification were used to build up Co-MOF on its surface: 1) deposition of Co-containing precursor through wetness impregnation method with aqueous $Co(NO_3)_2$ solution followed by calcination and 2) preparation of amino-functionalized silica through grafting of (3-aminopropyl)trimethoxysilane (APTMS). The textural data confirmed the uniform covering of the silica surface with the APTMS. At the same time, the irregular filling of silica pores was observed in the case of cobalt oxide-coated silica.

Cobalt imidazolate framework was synthesized according to the reported procedure [3]. The BET surface area of the obtained sample was 504 $m^2/g$. The pore size distribution curve had two maximums corresponding to two types of pores (1.1 and 2.2 nm in diameter). Deposition of Co-MOF on modified silica surface was carried out under the same solvothermal conditions in the presence of the corresponding silica samples. Successful formation of Co-MOF phase on the amino-modified silica was confirmed by low-temperature $N_2$ adsorption study, XRD data and FT-IR spectroscopy, while Co-MOF did not grow up on cobalt oxide-coated silica surface. In the last case, a homogeneous nucleation of MOF predominated.

The NHPI was immobilized into pores of Co-MOFs/APTMS-$SiO_2$ by impregnation procedure from the solution. The selective localization of NHPI inside the pores of the MOF was confirmed by the significant decreasing of micropore volume of the obtained hybrid material in comparison with Co-MOFs/APTMS-$SiO_2$. The FI-IR spectrum of NHPI@Co-MOFs/APTMS-$SiO_2$ revealed the characteristic bands of all components of the hybrid material. The catalytic activity were tested in selective oxidation of cyclohexane.

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# The synthesis of palladium catalysts on modified silica and alumina

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Typical large-scale fields applications of supported catalysts are fine organic synthesis, industrial synthetic processes of petrochemicals and pharmaceuticals [1, 2]. The processes of liquid phase hydrogenation of substituted nitrobenzenes is essential and clean technologies for the production of various aromatic amines, which are key intermediates for manufacturing agrochemicals, isocyanate, pharmaceuticals and dyes. The most common catalysts of hydrogenation used are platinum group metals such as palladium, platinum, iridium and etc. Nanometer palladium clusters have enormous potential for catalysis. However, the loss over time of catalytic activity and/or selectivity is a problem of great and continuing concern in the practice of industrial catalytic processes. Therefore, the development of hydrogenation catalysts is an important task.

The Possible ways of solution is include a search of synthesis methods, change of reaction conditions, alloying by different chemical elements and compounds, selection of supports and modification of catalyst surface.

And the most interest was excited the modification of surface. In particular, the idea was appearing, that the functional groups on support surface may be influence on electronic state of supported metal.

The silica was modified by the aminopropil groups, because amine (-$NH_2$) groups is very comfortably for further nucleophilic substitution by other chemical groups with different applications. And the alumina was modified by nitric acid treatment.

Palladium catalyst was prepared by drop-wise addition of 0.1 M $H_2PdCl_4$ (during 10 min) to a support powder suspended in aqueous $Na_2CO_3$ (molar ratio = $Na_2CO_3$:$H_2PdCl_4$ was attained 10:1).

The qualitative composition of the surface of the catalyst was studied by diffuse reflectance IR spectroscopy. Pulse chemisorption analysis was carried out to determine the chemically active surface area, the dispersion of the metal, and the active particle size by applying a pulsed titration of the sample with a chemically active gas. The morphological characteristics of supports and catalysts were examined by scanning electron microscopy. For determination of the elements chemical state, qualitative and quantitative analysis was used the XPS study of supports and catalysts. The influence of acid-base properties of supports on activity and stability of catalysts was studied by temperature-programmed desorption method.

Also, the catalytic tests were carried through the liquid hydrogenation of p-nitroaniline. As solvent was taken the water solution of 2-propanol (0.68 mol share). The kinetics of reaction was measured using hydrogen uptake. Obtained dependences of absorbed hydrogen on time is characterized the linear shape of kinetic curves. This may to means that the partial reaction order with respect to hydrogen is zero. So, a reaction rates were calculated from kinetic curves via the tangent of inclination angle of hydrogen uptake curve (Table 1). In addition, the values of the observed reaction rates were assigned to the unit mass of the deposited metal. Deactivation of catalysts were studied under conditions of p-nitroaniline hydrogenation to 1,4-phenylenediamine in 2-propanol with repeat of injecting of p-nitroaniline at the end of reaction. In total, 5 repeated reactions were carried out on each catalyst.

As result were established the next facts. The catalysts on alumina more active then catalysts on silica. But the catalysts on silica more stable, then the catalysts on alumina.

This is may be to explained by the acid centers on alumina. The catalyst activity is increased with increase the acid nature of support surface. The XPS study showed the chemical state of palladium supported on silica was not change. But the metal on alumina was oxidized.

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# Development, synthesis and investigation of titania-zirconia nanomaterials for application in microcapillary reactors

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Ordered mesoporous titania-zirconia $Ti_xZr_{1-x}O_2$ composites were synthesized by self-assembly using titanium isopropoxide and zirconium oxychloride as precursors and amphilic triblock copolymer F127 as a template [1]. The self-assembly process proceeds without the addition of acid, which is necessary to preserve the morphology and structure of the catalytic nanoparticles. A number of samples were prepared by varying the Ti content from 0 to 100% (designated as 0Ti, 15Ti, 30Ti, 70Ti, 100Ti). In the low angles region, a peak near $1.63^0$ is observed in diffractograms, indicating ordered structure of pores. According to high angle X-ray diffraction data, the anatase phase peaks (JCPDS 71-1169) are present in pure $TiO_2$. Increasing Zr content inhibits crystallization, since the samples of 15 Ti, 30Ti, and 70Ti are in an amorphous state. Samples with high Zr content contain mainly the tetragonal phase of $ZrO_2$ (JCPDS 17-0923) and traces of the monoclinic $ZrO_2$ phase (JCPDS 37-1484). After oxidative treatment at 600 °C, the mesostructure of 70Ti is destroyed, while the mesostructures of samples with a higher Zr content are retained (30Ti and 15Ti). In the high angles diffractograms the sample 15Ti after oxidation at 600 °C contains the orthorhombic phase $ZrO_2$ (JCPDS 34-1084); the sample 70Ti contains the phases $Ti_2Zr_2O_6$ (JCPDS 46-1265) and $Ti_7Zr_5O_{24}$ (JCPDS 34-209); the sample 30Ti is amorphous. When the temperature is increased to 600 °C, the peaks become narrower and more intense. For samples 15Ti and 70Ti, the crystallite size increases from 1.4 nm to 17 nm and from 1.2 nm to 17 nm, respectively. The growth and increase in the size of crystallites leads to the destruction of mesostructures. For the 30Ti sample, this change is less pronounced, with the particle size calculated by the Scherrer equation increasing from 1.3 to 1.5 nm. After calcination at 800 °C, the pore walls crystallize to $ZrTiO_4$ (JCPDS 34-0415). It is obvious that crystallization leads to the destruction of the mesoporous structure due to the phase transformation and the rapid growth of nanocrystallites. The structure of pore walls and their thermal stability are systematically studied by transmission electron microscopy and low-temperature adsorption of nitrogen. Composites possess an ordered pore mesostructure, a high specific surface area (up to 157 $m^2/g$), a large pore volume (0.13-0.21 $cm^3/g$), and a uniform pore size distribution (3.6-3.7 nm). This approach can be used to develop an ordered mesoporous catalytic coating for use in microcapillary reactor.

The coatings of 1.7 wt.% $PdZn/TiO_2$ and 1.4 wt.% $PdZn/Ti_{0.8}Zr_{0.2}O_2$ (molar ratio Pd/Zn 1/1) on the inner surface of a capillary reactor 0.53 mm in diameter, 10 m in length were synthesized. The coatings were tested in selective hydrogenation of 2-methyl-3-butyn-2-ol at 333 K and 1 atm $H_2$. The yield of the product of 2-methyl-3-buten-2-ol was 3.6 and 5.8 g/day, selectivity was 97.1 and 97.2% at 98% conversion on $PdZn/TiO_2$ and $PdZn/Ti_{0.8}Zr_{0.2}O_2$ coatings, respectively.

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# SECTION 2

## PROMISING CATALYTIC PROCESSES

# Partial oxidation of dimethyl ether to hydrogen-rich gas over $Ce_{0.75}Zr_{0.25}O_2$-supported Pt, Ru or Rh catalysts

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Analysis of current literature [1-3] shows that DME which can be synthesized directly from synthesis gas will play an important role in energy transfer. Thus hydrogen-rich gas produced by PO DME [2, 3], seems to be very attractive for fuel cells and other applications.

Overall PO DME is expressed by equation:

$(CH_3)_2O + 0.5O_2 = 2CO + 3H_2$

Studies of PO DME are at the initial stages, and only a few works are available. It is generally assumed that PO DME over supported metal catalysts occurs by the sequential kinetic scheme via the stage of the formation of methane, followed by steam/dry reforming of the formed methane to hydrogen-rich gas.

The present work reports the performance of the $Pt/Ce_{0.75}Zr_{0.25}O_2$, $Ru/Ce_{0.75}Zr_{0.25}O_2$ and $Rh/Ce_{0.75}Zr_{0.25}O_2$ catalysts in PO DME to hydrogen-rich gas to be used for fuel cell feeding.

The catalysts (granule diameter 0.25 – 0.5 mm) in amount of 0.1 μmol/g (1 wt. % Ru and Rh, 1.9 wt. % Pt) were prepared by the method of sorption-hydrolytic deposition. The samples were dried and reduced in hydrogen flow at 250 °C for 30 min. The BET specific surface area of the prepared catalysts was close to that of the $Ce_{0.75}Zr_{0.25}O_2$ support 70 $m^2$ $g^{-1}$. The catalyst was characterized by TPO, XRD, TEM CO chemisorption techniques.

DME PO was performed in a fixed bed flow quartz reactor at atmospheric pressure, temperature 200-700 °C GHSV=10000 $h^{-1}$, $DME:O_2:N_2 = 30:15:55$ (vol. %). The composition of the inlet and outlet gas mixtures were analyzed by GC equipped with TCD/FID and Porapack T/molecular sieve (CaA) columns.

The results obtained prove $Ru/Ce_{0.75}Zr_{0.25}O_2$, $Rh/Ce_{0.75}Zr_{0.25}O_2$ and $Pt/Ce_{0.75}Zr_{0.25}O_2$ to be efficient catalysts for PO DME to hydrogen-rich gas. For instance, the $Pt/Ce_{0.75}Zr_{0.25}O_2$ catalyst provided the hydrogen productivity and yield of ~6 L $H_2/(g_{cat}\cdot h)$ and ~ 80 %, respectively, under experimental conditions: T = 700 °C, P = 1 atm., and GHSV = 10000 $h^{-1}$ for $DME:O_2:N_2 = 30:15:55$ (vol. %). Besides, the catalyst showed good stability at 650 – 700 °C.

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# Study of the Structure and Optical Properties of $TiO_2$ Prepared via Pulsed Laser Ablation for Photocatalytic Applications

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The nanodispersed titanium dioxide is currently widely used in photovoltaic devices that find application in the green solar energy technologies, as well as in production of bactericidal materials and sunscreen creams. However, it is the heterogeneous photocatalysis that holds the most promise as a field of its application.

Currently, new technologies to synthesize titania-based materials, which absorb light in the visible region and have high photocatalytic activity, are developed. Pulsed laser ablation (PLA) has attracted a great interest, since this technique allows obtaining pure nanocolloids and nanocrystalline powders during ablation in liquids or vacuum or gaseous media. Despite a lot of research, there is not enough knowledge about structure and properties of the titanium dioxide synthesized by PLA method. This is due to the difficulties associated with obtaining a sufficient amount of ultrafine powder for research.

$TiO_2$ powder were synthesized using Nd:YAG laser (wavelength of 1064 nm, frequency of 20 Hz, pulse duration of 7 ns). Some of the samples were annealed at temperatures of 100 - 1000 °C.

The initial $TiO_2$ is a dark blue powder consisted of spherical crystallites with an average size of 5-10 nm and an insignificant number of large particles with a size of up to 80 nm. After annealing the sample changes color to light grey at 400°C and becomes white at 600°C. According to XRD data and Raman spectroscopy, the material is nanocrystalline and consists of phases of anatase and rutile. Also it should be noted that this method of preparation allows obtaining nanoparticles with anatase phase more resistant to temperature effects.

X-ray photoelectron spectroscopy data shows that only the doublet with bond energy of 458.5 eV (Ti2p3/2) corresponding to $Ti^{4+}$ state. Photoemission spectra from level $O_{1s}$ with subsequent deconvolution gives two peaks with bond energies 529.7 eV which corresponds to lattice oxygen of titanium dioxide and 531.9 eV belongs to adsorbed oxygen on the surface of titanium dioxide.

It was found that $TiO_2$ diffuse reflection spectra had an intense additional absorption in visible region. This additional absorption is due to the presence of defects of various nature in the structure of $TiO_2$, namely, different types of oxygen vacancies. (F, $F^+$ and $F^{2+}$-centers). These $F^+$ and $F^{2+}$ defect states can act as traps captured photoexcited electrons, that increases the charge carriers lifetime and prevents their recombination [1]. It was found that with an annealing temperature increase, the number of defective states decreases. This affects the absorbtion intensity in the visible region, and also affects the color of the samples. The calculated band gap was 2.65 eV. Decrease in the band gap value is due to the presence of defect levels in the band gap that lie higher in terms of energy than 2pO levels forming the valance band of $TiO_2$. Therefore, the defect levels blur the clear boundary of the valance band, and they appear as additional absorption in the visible spectrum. It was found that with an annealing temperature increase, the number of defective states decreases. This affects the absorption intensity in the visible region, and also affects the color of the samples.

Thus, by pulsed laser ablation, we have prepared nanocrystalline titanium dioxide witch absorbs intensively in the visible range of spectrum, and can be used for photocatalytic applications.

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# Study of physicochemical and photocatalytic properties of ZnO nanopowders obtained by pulsed laser ablation

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Today, zinc oxide nanoparticles (NPs) have emerged as an efficient and promising material in different fields because of its unique properties [1]. The heterogeneous photocatalysis is attractive technology for the accumulation and conversion of solar energy for a wide range of environmental applications, such as disinfection, decolorization and purification of air and water. Along with the most studied titanium dioxide $TiO_2$ in this field, ZnO is the closest alternative to it. Zinc oxide is a direct bandgap semiconductor with the band gap about 3.2-3.7 eV. The disadvantage of ZnO is that it absorbs light only in the UV region and only small fraction about 4-5% of the solar spectrum contains this range. Therefore, effective conversion of solar energy is still a problem. Various strategies have been employed to improve the photocatalytic efficiency of ZnO under visible light [2]. Doping by noble metals affects the rate of phase transfer of electrons and recombination of charge carriers due to the formation of new electronic traps, and also promotes the sensibilizatization of ZnO to the visible region of the spectrum. Pulsed laser ablation (PLA) has recently become a convenient, simple, effective and versatile approach to prepare different nanomaterials [3].

The aim of this work is to study the structure, morphology, optical and photocatalytic properties ZnO obtained by PLA of Zn metal target (99.99%) in water and air atmosphere, as well as powders modified with silver and gold (ZnO/Ag and ZnO/Au).

To obtain the initial ZnO powder a pulsed nanosecond Nd: YAG laser (1064 nm, up to 200 mJ, 7 ns, 20 Hz) was used. ZnO/Me (Me – Ag and Au, 10 mol.%) samples were prepared by impregnating ZnO nanopowders by aqueous $AgNO_3$ and $HAuCl_4$ solutions respectively and dried at 60 °C. Obtained initial ZnO and ZnO/Me samples were also annealed at 300 and 500 °C in a muffle furnace (with heating rate 10 °C/min) for 4 hours.

The phase composition of the powders was determined by X-ray diffraction patterns obtained with a Shimadzu XRD 6000 in the range of $2\theta$ = 10-70° with a scan rate of 2 °/min. The morphology and shape of ZnO NPs was investigated by transmission electron microscopy (TEM, Philips CM 12). Optical properties were examined using Cary 100 Varian spectrophotometer in the range from 200 to 800 nm. Photocatalytic activity of the powders was evaluated using $1.75\times10^{-5}$ M aqueous solutions of organic dyes such as Rhodamine C and Methylene Blue upon light irradiation of Philips Master CDM-TD 70W/942 lamp ($\lambda$ = 320-800 nm). Optical glasses WG305 (UV-visible) and GG410 (visible $\lambda > 410$ nm) was used to investigate photocatalytic activity of obtained nanopowders depending on the irradiation light. The loss of the dye's concentration was evaluated by spectrophotometric measurements.

According to the XRD data initial ZnO nanopowder obtained PLA in air atmosphere has strong reflections of ZnO wurtzite phase, small amount of monoclinic $Zn_5(NO_3)_2(OH)_2(H_2O)_2$ and metallic Zn. ZnO obtained in water has no inclusion and consist only wurtzite phase. Modification ZnO lead to form Ag and Au NPs and strong XRD peaks were detected at higher annealing temperatures. UV–vis absorption spectra of ZnO and ZnO/Me samples clearly display an absorption in the UV region attributed to the band edge of ZnO and that in the visible region correspond to the localized surface plasmon absorption of Me nanoparticles respectively. As a result, modified nanopowders have better photocalalytic activity compared ZnO but annealing lead to decrease for dyes degradation possibly because of healing of defects and grain size growth.

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# Ni/$La_2O_3$ catalysts for dry reforming of methane: effect of synthesis conditions on the structural properties and catalytic performances

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Dry reforming of methane (DRM) is highly endothermic ($\Delta H^\circ_{25^\circ C}$ = 247 kJ/mol) and normally requires temperatures above 700°C to attain good conversion levels [1]. Nickel is the most frequently reported metal in DRM because of its good catalytic activity and its cost-effectiveness as compared with Rh, Ru, Pt, and Pd-based catalysts [2]. However, the main drawback of Ni based catalysts is represented by the production of significant amount of carbon and by the sintering at the high temperatures of the reaction. Carbon deposits are formed when the rate of methane dissociation is faster than the oxidation of carbon by the surface oxygen species arising from $CO_2$ dissociation on the metal component or from carbonates formed at the metal support interface [3, 4]. Until now, many studies have demonstrated that metal oxides such as $CeO_2$, MgO, $ZrO_2$ have positive effects on catalytic activity, stability and carbon suppression of nickel catalysts for DRM [5, 6].

In the present work the physical chemical properties, the related catalytic activity and the long-run stability of Ni-$La_2O_3$ catalysts have been evaluated in DRM reaction. The aim was to investigate the effect of ammonia addition during the synthesis of $La_2O_3$ oxide carried out by sol-gel method in presence of citric acid. Ni(10%wt) was deposited by wetness impregnation over two $La_2O_3$ oxides prepared with and without adding $NH_3$ solution during the synthesis, the corresponding catalysts were labelled as *Ni-La CA* and *Ni-La CA-$NH_3$,* respectively. The so far prepared catalysts were characterized by BET, XRD and TPR techniques. The XRD patterns of the supports calcined at 800 °C showed that ammonia addition favors the formation of $La_2O_3$ phase with respect to $La(OH)_3$. $La_2O_3$ was the only lanthanum phase detected in the XRD pattern of *Ni-La CA-$NH_3$*, after calcination at 600 °C and reduction treatment at 700 °C, moreover, weak features attributed to dispersed metallic Ni particles were found. While in the case of *Ni-La CA*, both phases, $La_2O_3$ and $La(OH)_3$ were present along with well visible peaks of metallic Ni suggesting the presence of big clusters. DRM gradient catalytic test performed between 400°C to 800°C revealed higher catalytic activity of *Ni-La CA*, nevertheless long run test showed a better stability of *Ni-La CA-$NH_3$* catalyst. The spent catalysts were characterized by XRD, TGA, Raman and TEM analyses. In both samples $La_2O_2CO_3$ phase was formed together with C graphite peak of higher intensity in the case of *Ni-La CA* in agreement with greater weight loss revealed by TGA and stronger deactivation during long run with respect to *Ni-La CA-$NH_3$*. The effect of the nature of the catalyst on the amount of carbon coke formed during DRM was also confirmed by Raman and TEM results.

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# Impact of Surface Acid and Sulfo Groups on the Activity of Sibunit Carbon Catalysts in the Depolymerization of Cellulose to Glucose and 5-HMF

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Glucose and 5-HMF are well known to be valuable chemicals. They are promising for chemical industry (plastics and pharmaceutics) and fuel production. Utilization of inedible cellulose as an alternative raw material, non-corrosive solid acid catalysts and one-pot design of the process let one to overcome the drawbacks of the traditional technologies of glucose and 5-HMF production. Sibunit carbon material seems to be very promising to design a solid catalyst for cellulose depolymerization into glucose and 5-HMF due to significant mechanical strength and high specific surface area. However low surface acidity of Sibunit makes additional modification of the carbon indispensable to increase the amount of acid groups on the catalyst surface. Ten Sibunit carbon catalysts were prepared via sulfonation ($H_2SO_4$ at 80-200 °C), oxidation (by $HNO_3$ or wet air) and subsequent oxidation-sulfonation. **The aim** of this work was to develop the solid acid catalysts based on Sibunit for the production of glucose and 5-HMF from cellulose and to evaluate the influence of acid and sulfo groups on the carbon surface on the production of the target products and product yields.

The catalysts were characterized by $N_2$ absorption, titration with NaOH, XPS and XRF. XPS analysis confirmed the chemical bonding of surface groups with carbon and revealed the amount of acid and sulfo groups on the catalyst surfaces. XRF revealed high stability of the materials developed under hydrothermal conditions (upto 200 °C). According to XPS, the sulfonated and oxidized-sulfonated carbons contained both sulfo and acidic groups while oxidized samples had just acidic groups. The amount of sulfo groups formed by subsequent sulfonation of oxidized materials was lower by the factor of two compared with sulfonated Sibunit.

The catalysts were tested in the one-pot hydrolysis-dehydration of cellulose in both batch and flow reactors at 180-200 °C under inert atmosphere. The results obtained make possible to assume a heterogeneous reaction mechanism: saccharide transformations take place on the surface of catalyst. Specific surface aria, the surface acidity and the nature of the surface groups are crucial parameters for the activity of solid Sibunit acid catalyst.

Flow experiments demonstrated the distribution of all the Sibunit catalysts into three groups in terms of the activity. Untreated pure Sibunit was only one catalyst in the group with the lowest activity (glucose yield 20 %). The second group consisted of sulfonated and oxidized catalysts. Carbon oxidized by wet air was the most active carbon in spite of the lowest acidity among all the samples in the group due to high specific surface area. Oxidized and sulfonated Sibunit samples demonstrate mediate activity in 5-HMF production. The third group was composed of oxidized-sulfonated carbons which produced glucose with high 67-75 % yields. They were noticeably (about 1.5-2 times) more active in glucose formation compared to other catalysts and such a difference of the activities was in the agreement with the total acidity of the catalysts. However, oxidized-sulfonated Sibunits had the lowest activity in 5-HMF production.

As a whole testing all the catalysts revealed the following. 1) Both acid and sulfo groups are active in cellulose hydrolysis to glucose. The activity and the surface total acidity increased simultaneously. 2) Additional sulfonation of oxidized carbons caused significant increasing the catalyst activity in the hydrolysis process (sinergetic effect of acid and sulfo groups). 3) The activity of sulfo groups is noticeably high in glucose dehydration to 5-HMF. Decreasing the amount of sulfo groups diminished 5-HMF yields.

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# The effect of chlorine and fluorine in platinum-zeolite catalysts on the isomerization of n-heptane

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By the beginning of 2018, the content of aromatic hydrocarbons in commercial motor gasoline is regulated in 123 countries. Thus, in Russia, according to the requirements of the Technical Regulations of the Customs Union, the content of aromatic hydrocarbons should not exceed 35 % vol., including benzene not more than 1 % vol. [1]. In Russia, the key source of high-octane components of commercial gasoline is the reforming process, in which products the content of aromatic hydrocarbons can reach 80% wt., and the benzene content is 5% wt. As a result, modern enterprises for the production of gasoline that meet the requirements of technical regulations should have additional processes that allow obtaining non-aromatic high-octane components of gasoline.

One of such processes is the isomerization of paraffins of normal structure. In Russia over the past 10 years, the number of isomerization units in operation and under construction has doubled, and the content of branched paraffins in commercial gasoline has increased from 5-10 % to 12-15 % wt. [2, 3].

At present, the isomerization of pentane-hexane fractions is widely distributed at oil refineries. The catalysts of this process are sulfated zirconia, zeolite-containing and fluorinated alumoplatinum catalysts, chlorinated alumina. In the last two catalysts, fluorine and chlorine are the main sources of Lewis acid sites. The use of fluorine and chlorine as an acid component has also been widely used in the production of reforming catalysts.

A relatively new and promising process is the isomerization of n-heptane. The main feed for one is the straight-chain or recovered from the reformate heptane fraction 70-105 °C. As catalysts, systems based on molybdenum oxide, tungstate-containing or sulfated zirconia, borate-containing systems and systems based on zeolites are examined.

The aim of this work was to study the effect of fluorine and chlorine in platinum zeolite-containing catalysts on the isomerization reaction of n-heptane. For this purpose, halogens were introduced into the catalysts from hydrofluoric and hydrochloric acids, respectively, in various amounts and at different stages of synthesis. The carriers were a mixture of zeolite BEA and alumina in a ratio of 30 to 70 % wt. Platinum was deposited from hexachloroplatinic acid $H_2PtCl_6$ in an amount of 0.3 % wt. The main criteria for assessing the effectiveness of catalysts were the operating temperature, the yield of the target products and the selectivity for the target products.

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# Oil residues decomposition by $Fe_2O_3$-based nanoscale catalytic systems

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Nanoparticles efficiency in laboratory oil refining has been discussed for the last decade [1]. Application of conventional catalysts for thermal decomposition of heavy hydrocarbon residues is limited with the formation of coke and metals on its surface. Moreover, conventional cracking in catalysis is considered to be unreasonable when test Conradson carbon residues of petroleum products more four percentages (ASTM D189) [2].

There are catalytic systems developed to decompose hydrocarbons with cocking behavior of 10% and metal, vanadium and nickel, concentration till 30…50 $mg \cdot kg^{-1}$ [3]. Nevertheless, these catalysts have not still been introduced into practice due to its high cost. Meanwhile, the use of traditional catalysts may be rationally replaced by highly dispersed additives initiating thermolisys of heavy hydrocarbon residues.

In our work we examined the influence of iron oxide nanoparticles dispersed in hydrocarbon external phase on thermal decomposition of oil residues. Nanoparticles were synthesized via two stages. Primarily, nanopowder of $Fe_3O_4$ with average particles size of 10 nm was obtained by impulse laser ablation of iron target prior, then powder heating at 500°C in air atmosphere. As a result we had nanoparticles of hematite $Fe_2O_3$ with average size of 30 nm. Then nanoparticles were dispersed in gasoil stock with anionic surfactant. The introduction of nanoparticles suspensions into oil residues was accompanied with mixing. The content of hematite particles in oil was 0.05…0.2 wt.%. Thermolysis of samples was conducted at 435°C during an hour under the conditions chosen in previous experiments [4].

It has been experimentally shown, application of iron oxide nanoparticles for thermal oil residues refining allows additionally obtaining 45…57 wt.% of fuel fractions.

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# Oxidative dehydrogenation of ethane-ethylene fraction

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Actually, the ethane-ethylene fraction (EEF), along with a mixture of other light hydrocarbons presented in refinery gases, is usually burned to produce heat. An interesting use of EEF can be the production of isopropyl alcohol - an environmentally safe high-octane component of motor fuels [1]. The first stage of the proposed method is the synthesis of ethylene. Oxidative dehydrogenation of ethane (ODE) can be an alternative to steam cracking for ethylene production [2]. The most effective catalysts for ODE reaction are multicomponent compositions based on mixed oxides of molybdenum and vanadium [3].

The aim of the work is to study the effect of an ethylene admixture in the ethane-ethylene fraction on the oxidative dehydrogenation of ethane on the VMoTeNb oxide catalyst.

The $Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_n$ catalyst was synthesized from aqueous slurry using ammonium heptamolybdate, ammonium metavanadate, telluric acid and niobium oxalate. The prepared slurry was spray-dried at 220 °C and heated in an air flow at 300 °C during a short period and in He at 600 °C for 2h. The main phase of the prepared catalyst is the orthorhombic phase M1 (≥85% by weight), the most active in the oxidative conversion of ethane to ethylene [4]. The oxidative dehydrogenation of EEF (ODEEF) was carried out at atmospheric pressure in a fixed-bed tubular reactor at 330-450 °C and contact time 0.5-0.25 s. Fraction size of the samples was 0.25-0.5 mm. The feed consists is EEF:air = 15:85 (vol. %). The ethylene content in the EEF is 20% vol., which corresponds to the composition of the ethane-ethylene fraction of the hydrocarbon off-gases of JSC Gazpromneft-MNPZ. The oxidative transformations of the individual components included in the EEF (ethane and ethylene) were carried out for comparison. The content of hydrocarbons in the initial reaction mixture corresponded to their content in EEF, ratio oxygen/hydrocarbon = 1, temperature 400 °C.

Comparison of ODEEF with the reactions of oxidative ethane dehydrogenation and ethylene oxidation carried out under similar concentration and temperature conditions, shows that ethylene does not noticeably influence the ethane conversion. At that, ethane strongly suppresses the ethylene conversion. This can be due to the competitive adsorption of ethylene and ethane on the same active catalyst centers and a greater reactivity of ethane.

The maximum ethylene yield from the ethane-ethylene fraction is close to that reached in ethane oxidatative dehydrogenation 70-72%. The negative influence of ethylene admixture in the ethane-ethylene fraction, expressed in an increase in selectivity to carbon oxides and a reduction in the yield of ethylene, is observed at ethane conversion above 90%.

So, the principle possibility of using EEF without separation into separate components for the production of ethylene with a yield of 70-72% has been confirmed.

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# Role of the sacrificial agents in the evolution of the phase composition of photocatalyst $Cd_{0.3}Zn_{0.7}S$ modified with zinc hydroxide during the photocatalytic hydrogen production

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Considering the depletion of the world’s fossil-fuel reserves and its uneven distribution, hydrogen-based energy systems have attracted extensive attention. One of the most interesting ways of hydrogen production is photocatalytic water splitting with sacrificial agents such as inorganic (aqueous $Na_2S/Na_2SO_3$ solutions) and organic compounds. Earlier it has been shown that the most active photocatalysts for these donor system contain $Zn(OH)_2$ and $Cd_xZn_{1-x}S$ phases [1-3]. The reaction media is known to affect the surface state of a catalyst and it catalytic activity [4]. From fundamental and practical points of view, it is important to study the effect of the reagent nature on the photocatalyst composition and changes in its catalytic activity value.

In this work y-$Zn(OH)_2/Cd_{0.3}Zn_{0.7}S$ and 1% Pt/y-$Zn(OH)_2/Cd_{0.3}Zn_{0.7}S$ photocatalysts (where y is a weight content of zinc hydroxide, y = 10, 20, 30, 40, 50) were prepared by the impregnation method and tested in the photocatalytic hydrogen production from aqueous solutions of $Na_2S/Na_2SO_3$ and ethanol, respectively, under visible light irradiation ($\lambda = 450$ nm). For both sacrificial agents the reaction rate went through a maximum with the increase of the $Zn(OH)_2$ content. The most active samples were 20-$Zn(OH)_2/Cd_{0.3}Zn_{0.7}S$ (for inorganic system) and 1% Pt/10-$Zn(OH)_2/Cd_{0.3}Zn_{0.7}S$ (for ethanol solution).

We measured the hydrogen production rate on the most active samples and the samples with high $Zn(OH)_2$ content during four irradiation cycles. Every cycle lasted 90 min. It has been demonstrated that for all photocatalysts the reaction rate increased with the growth of the irradiation cycle number. The highest values of the catalytic activity were equaled to 8.9 mmol $g^{-1}$ $h^{-1}$ for 20-$Zn(OH)_2/Cd_{0.3}Zn_{0.7}S$ (aqueous $Na_2S/Na_2SO_3$ solutions) and 3.2 mmol $g^{-1}$ $h^{-1}$ for 1% Pt/10-$Zn(OH)_2/Cd_{0.3}Zn_{0.7}S$ (ethanol solution).

The phase composition of the samples with high $Zn(OH)_2$ content (30-$Zn(OH)_2/Cd_{0.3}Zn_{0.7}S$ and 1% Pt/30-$Zn(OH)_2/Cd_{0.3}Zn_{0.7}S$) was studied by the X-ray diffraction method before and after irradiation. The XRD method showed that zinc hydroxide transformed incompletely to cubic zinc sulphide under irradiation in aqueous $Na_2S/Na_2SO_3$ solutions. This process may be realized from the $Zn(OH)_zS_{1-0.5z}$ formation which are known to be activated under visible light illumination [5] and may take part in the heterojunctions of the photoinduced charge carriers that improve the separation of electrons and holes and the catalytic activity values. The 1% Pt/30-$Zn(OH)_2/Cd_{0.3}Zn_{0.7}S$ photocatalyst has also change its phase composition under photocatalytic hydrogen production from ethanol. The XRD method demonstrated that β-$Zn(OH)_2$ transformed to ε-$Zn(OH)_2$ which can be involved in the heterojunctions of the photoinduced charge carriers with the highest efficiency [3].

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# The peculiarity of genesis and properties of Ni-Ce-La mixed oxide catalysts

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High activity, wide availability and low cost of Ni metal catalysts make them attractive for large-scale applications in hydrogenation and reforming reactions [1]. The use of the Ni catalysts with well-stabilized small nanoparticles of the active metal has a number of significant advantages: higher active surface area and developed metal-support interface, an advanced intrinsic activity and a lower rate of carbon formation. The high dispersion of the active component can be achieved through the application of structural promoters, the use of the confinement effect or realization of a strong metal-support interaction [1-3]. The limiting case of the deep interaction between the nickel and the support is the formation of new phases at the support-metal interface or a combined bulk phase. In this case perovskites, hydrotalcite and other mixed oxides are used as precursors of Ni catalysts. Their activation in the reducing atmosphere leads to the destruction of the original structure and the formation of highly dispersed $Ni^o$ particles on the oxide matrix.

In this work, with the aim to develop a Ni catalyst with the superior anti-sintering and anti-coking behavior, the peculiarity of genesis and properties of Ni-Ce-La mixed oxide materials were studied. To consider the features of a mixed oxide as the catalyst precursor, the characteristics of $(CeLa)_{0.8}Ni_{0.2}O_y$ materials prepared by the polymerizable complex method were compared with those of $Ni/Ce_{1-x}La_xO_y$ systems obtained by the impregnation method.

The $(CeLa)_{0.8}Ni_{0.2}O_y$ materials with different La/Ce molar ratio (0, 0.25, 1, 4) were synthesized by the polymerizable complex methods and calcined at 300, 500, 700 or 900ºC. The $Ni/Ce_{1-x}La_xO_y$ samples ($x = 0, 0.2, 0.5, 0.8, 1$) were prepared by the incipient wetness impregnation method. The Ni content is equal to 10 wt. %. The TG-DTA, BET, XRD, HRTEM-EDX and $H_2$-TPR methods were applied for catalyst characterization. Functional properties of samples were investigated in the reaction of autothermal reforming of ethanol (ATR of $C_2H_5OH$) at atmospheric pressure, temperature 200-700°C, a flow rate of 320 mL/min and the molar ratio between reagents $C_2H_5OH : H_2O : O_2 : He = 1 : 3 : 0.4 : 0.7$.

It was shown that the preparation method and La/Ce molar ratio influence on the textural, structural and redox properties of Ni-Ce-La mixed oxide materials. According to XRD data, the $CeO_2$ based solid solution with an average crystallite size of 4-6 nm is the main phase of $(CeLa)_{0.8}Ni_{0.2}O_y$ materials calcined at 300-500ºC. At an increase of calcination temperature up to 700-900ºC the NiO or $La_2NiO_4$ phases were also observed. The two-phase system – the $CeO_2$ based solid solution and NiO - was formed in case of $Ni/Ce_{1-x}La_xO_y$ samples. The crystallite size and NiO dispersion are strongly affected by La/Ni molar ration and conditions of thermal treatment. At an increase of La content the value $S_{BET}$ of samples decreases while NiO dispersion increases. The presence of La impedes the $Ni^{n+}$ reducibility. In particular, for $Ni/Ce_{1-x}M_xO_y$ the increase of x from 0 to 0.5 leads to the decrease of NiO particle size from 25 to the atomically dispersed state, while the temperature of $Ni^{n+}$ reduction increases from 340 to 380ºC.

The effect of the preparation method and conditions of thermal treatment of Ni-Ce-La mixed oxide catalysts on their coking resistance and functional properties in ATR of $C_2H_5OH$ was studied. The composition-structure-properties correlation was established.

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# The Hydrodeoxygenation of Vegetable Oil over Pt/$WO_3$-$Al_2O_3$ catalysts

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Hydrodeoxygenation of vegetable and animal oils/fats is a promising trend for producing environmentally diesel-range hydrocarbons. The process of hydrodeoxygenation on the scale of industrial production is presented by Neste oil (NExBTL) [1] and UOP-Eni (Ecofining) [2]. The treatment process involves the use of traditional hydrotreating catalysts Ni(Co)Mo(W) with producing of n-alkanes $C_{12}$-$C_{22}$ in the first stage and noble metal catalysts (Pt, Pd, Ru) in order to improve the low-temperature properties of the final product in the second stage. This significantly complicates the treatment process and ultimately affects the cost of fuel.

In this work, the Pt/$WO_3$-$Al_2O_3$ system is considered as catalysts for the hydrodeoxygenation of fats. Its whose acidity varies in a wide range depending on the content of the modifier (tungsten oxide). Tungsten oxide of varying amounts (0–30 wt. %) was deposited on $\gamma$-$Al_2O_3$ by mixing a pre-homogenized suspension of pseudo-boehmite with a known quantity of aqueous solutions tungsten salt. Ammonium metatungstate was used as tungsten source [3]. Platinum (0.5 wt. %) was deposited on $WO_3$-$Al_2O_3$ by wet-impregnation method. Hexachloroplatinic acid solution was used as platinum source. Prior to reaction, the catalyst was reduced in a flow of hydrogen. The catalysts were tested in a hydrodeoxygenation reaction of sunflower oil at a temperature of 380 ° C and a pressure of 4.0 MPa, a mass feed rate of 1 $h^{-1}$, a ratio of $H_2$: oil = 2500 $nm^3$:$m^3$.

Pt/$WO_3$-$Al_2O_3$ catalysts exhibit high catalytic activity in the process of hydrodeoxygenation of sunflower oil. The products of the transformation of the feedstock are a mixture of saturated and unsaturated hydrocarbons. $^{13}C$ NMR method confirmed the absence of oxygen-containing compounds in products. The first hours of "run-in" of catalysts are characterized by intensive cracking reactions and high gas (predominantly $C_4$) and hydrocarbons of the gasoline fraction yields.

The ratio of iso-/n-alkanes in the products goes up with the increase of the $WO_3$ content in the support, which reduces the pour point of the fuel. An increase in the $WO_3$ concentration causes a decrease in the dispersion of platinum in the catalyst, which leads to an increase in the content of alkenes in the products, which compensate for the loss of isoalkanes in the mixture. Many hours of experiments have shown that over time, the gradually catalyst surface coking, leading to an increase in the concentration of alkenes and the ratio of $C_n/C_{n-1}$ in the products of the process.

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# Oxidative desulfurization of diesel fraction on CuZnAlO catalysts

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Current strict requirements for ultra-low sulfur content (10 ppm) in liquid motor fuels demand novel approaches for ultra-deep desulfurization. The gas phase oxidative desulfurization (ODS) of motor fuels with air or oxygen, initially proposed for desulfurizing petroleum fractions, may become a new promising technology for removal of refractory sulfur compounds. The gas phase ODS process is poorly described in the literature [1]. Oxidative removal of diesel organosulfur compounds on Cu-$CeO_2$, Pt-$CeO_2$, and CuO-ZnO-$Al_2O_3$ catalysts was described in [2, 3]. Selective oxidation of sulfur-containing compounds to $SO_2$ in the presence of air occurs at 300°C and atmospheric pressure. So, on the base of literature data catalysts based on CuO-ZnO-$Al_2O_3$ composition are promising for further studies providing better results in the ODS of sulfur-containing fuels [4].

Earlier in articles [5-7], we described the CuO-ZnO-$Al_2O_3$ catalyst and found that it is active in the ODS process. The CuO-ZnO-$Al_2O_3$ catalyst was prepared by precipitation from a solution of Cu, Al, Zn nitrates with appropriate concentrations with a solution containing sodium carbonate and sodium hydroxide and subsequent modification by $BO_2^-$ and $MoO_4^{2-}$. The catalysts were tested at 300-430°C in the ODS process of a model hydrocarbon fuel containing mixtures of thiophene, dibenzothiophene (DBT) or 4,6-dimethyldibenzothiophene (DMDBT) in toluene and a straight-run diesel fraction containing thermostable sulfur compounds. Sulfur content was 0.1 and 0.5 wt. % respectively.

The main products of oxidation of these compounds were $CO_2$, $SO_2$, and oxidized hydrocarbon fuel. According to DTA-TG, FTIR and XPS data ODS proceeds via the stage of adsorption of sulfur-containing molecules, followed by their destruction and evolution of $SO_2$ into the gas phase. In case of strong interaction of sulfur-containing molecules with the catalyst active sites, the accumulation of sulfur on the catalyst surface takes place in the form of metal sulfides, polysulfides, and sulfates. During the ODS reactions, also carbon was accumulated in the catalyst.

The reactivity of different sulfur-containing compounds in ODS over catalysts increased in the following sequence: thiophene < DBT < DMDBT. The sulfur removal efficiencies as high as 80-90% were attained for ODS of DMDBT. The study of ODS process of straight-run diesel fractions on the catalysts showed that the highest removal of sulfur from fuel was 50% at 400°C. The study of the composition of the oxidized fuel shows that the derivatives of DBT are most easily removed. This result is similar to that found for the model hydrocarbon fuel. Therefore, the presence of methyl groups in sulfur compounds, especially in DBT does not have the inhibiting effect in the ODS reaction by contrast to the HDS process, but on the contrary, promotes the oxidation.

Thus, it can be concluded that the ODS process of the model and real hydrocarbon fuels on CuO-ZnO-$Al_2O_3$ catalysts was developed. It was determined that ODS proceeds via the stage of adsorption of sulfur compounds, followed by their destruction and evolution of $SO_2$. The reactivity of different sulfur-containing molecules in ODS over catalysts was shown to increase in the sequence: thiophene < DBT < DMDBT. The sulfur removal efficiency on the modified CuO-ZnO-$Al_2O_3$ catalysts from model fuels and straight-run diesel fractions was ca. 75% and 50% respectively.

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# Fe-Pillared layered aluminosilicates for catalytic aquathermolysis of heavy hydrocarbon feedstock

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Aquathermolysis in one of the key technologies decreasing viscosity and development of huge heavy oil reservoirs over the world. The catalytic aquathermolysis of heavy oils review includes applications of water- and oil-soluble catalysis based on transistion metals and traditional heterogeneous catalytic systems [1]. Pillared Clays (PILCs) are an interesting class of 2-dimensional microporous materials. Due to their high surface area, permanent porosity, enhanced texture and the presence of an active component in the interlayer spaces, combining both the carrier and the catalyst, PILCs are certainly promising in the field of heterogeneous catalysis. In particular it is possible to adapt the these systems for use in various catalytic processes by varying the composition of the complexes and the type of metals. The main directions of the pillar compounds production are the variation of the precursor (layered aluminosilicates), polyhydroxycations, intercalation conditions and intercalation [2-6].

In this work there were obtained Fe-pillared layered aluminosilicates by intercalation trinuclear acetate hydroxy-iron (III) chloride between the layers of Na-exchanged montmorillonite with following calcination at 450 ℃ in a tubular muffle furnace in oxidizing ($O_2$) and reducing ($H_2$) environments.

Elemental analysis, XRD, sorbtometry, Mössbauer spectroscopy and electron microscopy were used for Fe-PILCs characterization.

For catalytic activity of synthesised systems aquathermolysis of Ashal'cha oilfield heavy hydrocarbon feedstock were used. The experiments were carried out in 250 ml an autoclave at an operating pressure of 30 bar and temperature of 250 °C during 120 min. The catalysist/ feedstock ratio was 0.25 % mass. The analysis of reaction products was evaluated by distillation at atmospheric pressure. The results of experiments have showed that output of light gasoline fractions (with boiling point up to 200 ℃) in the control experiment was 1 %, with Fe-PILC catalysis calcined in $O_2$ environment – 3 %, with Fe-PILC catalysis calcined in $H_2$ environment – 5%.

Thus, the authors consider that pillared structures use in reactions of aquathermolysis of heavy hydrocarbons is very prospective.

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# Investigation of deactivation of the Pt/$MgAlO_x$ catalysts for propane dehydrogenation

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Platinum catalysts are promising systems for their use in the reactions of dehydrogenation of light and higher alkanes. Platinum catalysts are more active and selective compared with the systems based on chromium oxides. However, platinum based catalysts are rapidly deactivated. There are different ways of the deactivated catalysts regeneration: hydrogen or nitrogen purging, coke-burning treatment. But before applying certain kind of regeneration, it is necessary to understand the essence of the deactivation processes.

The aim of this work was synthesis of the Pt/$MgAlO_x$ catalysts (where layered double hydroxides were support precursor) with different platinum active sites localization, different platinum content and support basicity (different Mg/Al ratio); investigation of the catalytic properties of the catalysts in propane dehydrogenation at different temperatures and studying their deactivation processes.

MgAl-LDH were synthesized by traditional coprecipitatiom method by adding of magnesium and aluminum nitrates to sodium carbonate at constant pH = 10 and temperature = 60 °C. Thus LDH with preferential content of carbonate – anions in interlayer space of LDH were obtained (LDH-$CO_3$). Mixed oxides ($MgAlO_x$) were prepared by LDH-$CO_3$ calcination at 550 °C. «Activated» LDH with preferential content of OH – anions in interlayer space (LDH-OH) were made by mixed oxides rehydration in distilled water. Mg/Al ration in all supports was 2, 3 and 4. The platinum anchoring on selected supports was carried out by using of excess of $H_2[PtCl_6]$ solution. When adsorption of platinum complexes were on LDH-$CO_3$, active sites were formed on the outer surface of the support, and when complexes were anchored on $MgAlO_x$ or LDH-OH, platinum active sites were formed mainly in the interlayer space of the supports. Platinum content in catalysts was 0.3 and 1 wt. %. The concentration of metals in catalysts (after dissolution) was estimated by inductively coupled plasma atomic emission spectroscopy on a Varian 710-ES system. The catalytic properties of the systems were investigated in propane dehydrogenation (sample loading 0.5 g., the molar ratio $H_2/C_3H_8$ = 0.25, atmospheric pressure, feed space velocity of 8 g $h^{-1}$). The reaction temperature was 550, 590 и 620 °C. Before each experiment the samples were oxidized and reduced at 620 °C. Thermal analysis of deactivated samples was carried out at STA-449C Jupiter (Netzch) instrument. Platinum dispersion in catalysts was estimated by hydrogen chemisorption on AutoChem II 2920 («Micromeritics») device with thermal conductivity detector (TCD).

It was found that Mg/Al ratio in support, method of platinum anchoring and reaction temperature had a decisive influence on the Pt/$MgAlO_x$ catalysts activity and stability. Catalysts with high platinum content (1 wt. % Pt) possessed the activity closed to activity of samples with Pt content 0.3 wt.%. But 1%Pt/$MgAlO_x$ had lower selectivity of propylene formation. An increase in the Mg/Al ratio in the support led to a decrease in the activity of the catalysts, regardless of the platinum active sites localization. The effect of the reaction temperature on catalyst activity and stability was different, depending on the method platinum anchoring. Deactivation of Pt / LDH-OH catalysts increases with increasing temperature, while for Pt / LDH-$CO_3$ samples the reverse trend is observed. The increase of platinum content in the catalysts contributed to a decrease in their deactivation regardless of the reaction temperature.

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# Catalysts prepared by Pechini technique for low-temperature steam reforming of light hydrocarbons: correlations between composition and activity

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Nowadays many gas-and-oil producing companies in Russia face the problem of associated petroleum gas (APG) utilization. APG have variable composition (vol.%: 50-70 $CH_4$, 5-10 $C_2H_6$, 10-30 $C_{3+}$-hydrocarbons, 0-10 $N_2$, 0-10 $CO_2$) and can neither be pumped to pipelines due to high dew point temperature nor directly used as a fuel for internal combustion engines due to high calorific effect and detonation risk. Traditional gas refinery technologies are economically inefficient for low-debit and distant oil and gas fields. Therefore, an alternative way of APG utilization is necessary.

Low temperature steam reforming (LTSR) of light hydrocarbons represents a promising method of APG utilization. The process occurs at 250-350 °C and low steam to carbon ratio ($H_2O/C_{C2+}$ mol. < 1) Overall process can be described by two reactions: irreversible steam reforming of $C_{2+}$-hydrocarbons with the formation of $CO_2$ and $H_2$ followed by reversible $CO_2$ methanation:

1) $C_nH_{2n+2} + 2nH_2O \rightarrow (3n+1)H_2 + nCO_2$ (n > 1)
2) $CO_2 + 4H_2 \rightleftarrows CH_4 + 2H_2O$

As a result of this process, methane content increases which leads to decrease in the hydrocarbon dew point; also fuel characteristics of APG are improved which allows using the gas mixtures obtained in internal combustion engines for generating electricity directly on-site.

This work reports our results on synthesis and properties of Ni-based catalysts prepared by classic Pechini technique using metals nitrates, citric acid and ethylene glycol at molar ratio of 1:1:1. 30 wt. % NiO - 20 wt. % $MO_x$-$Al_2O_3$ (M = Mg, Cr, Ce) samples were synthesized in order to investigate the correlation between the composition of the catalyst and its catalytic activity in LTSR of a model propane-methane mixture. Industrial catalyst of CO and $CO_2$ methanation (38 wt. % NiO, 12 wt. % $Cr_2O_3$) and industrial $CH_4$ reforming catalyst (19 wt. % NiO) were chosen as reference samples.

It was shown [1] that catalytic activity increases in the following order: Industrial $CH_4$ reforming catalyst < Ni-$CeO_2$-$Al_2O_3$ ≈ Ni-$Cr_2O_3$-$Al_2O_3$ ≈ Ni-$Al_2O_3$ < Ni-MgO-$Al_2O_3$ ≈ Industrial CO and $CO_2$ methanation catalyst. Ni-Mg sample proved to be the most promising system having higher thermal stability as well as lower Ni content in comparison with the industrial catalyst.

CO chemisorption data showed that Ni-Mg catalyst had higher Ni specific surface area comparing to other catalysts prepared by Pechini technique. Thus, introduction of MgO into nickel-alumina catalyst significantly increased Ni dispersion and therefore catalytic activity in the LTSR of propane-methane mixture.

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# Influence of preparation method of Ag/$TiO_2$ composites on their photocatalytic properties

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Photocatalytic processes have drawn much attention from scientists all over the world since recent years. Ability to conduct many chemical reactions at room temperatures via different mechanisms is very promising for the development of science and industry. The most common photocatalyst to the recent time has been titanium dioxide [1], being able to effectively oxidize organic matter with the help of UV light and possessing a variety of notable advantages such as relative cheap price, lack of toxicity, and chemical stability. However, one major disadvantage of pure titania is its inability to be activated by visible light, which is more available due to its low energy and much greater presence in sunlight.

Various scientific groups have been conducting research in order to improve the activity of $TiO_2$ irradiated by the light of visible spectrum. Some of the known techniques are promotion by precious metal nanoparticles such as Au [2] or Ag [3], or modification of titania structure through creation of $TiO_2/SiO_2$ or $TiO_2/CeO_2$ composites [4]. In this work, promotion via metallic Ag is described, with the influence of preparation method on the resulting physical and chemical properties, such as optical absorption, catalyst structure, and photocatalytic activity being discussed.

Ag/$TiO_2$ photocatalysts were prepared via two different methods: impregnation in excess solution and photoreduction, with the sample series correspondingly named as Ag/$TiO_2$-IMP and Ag/$TiO_2$-PR. The support used for the deposition of Ag in both of the experiments was commercial $TiO_2$ Degussa P25. The amount of Ag in catalyst composition was varied.

The phase composition of the samples was investigated by X-Ray diffraction and FTIR spectroscopy. To study optical properties, UV-VIS diffuse reflectance spectroscopy was employed. To obtain metallic silver via the impregnation method, a TPR-$H_2$ method was also employed. Surface properties of the prepared samples were studied with the use of low-temperature $N_2$ method (BET). The photocatalytic activity of the samples was investigated in model experiments of Rhodamine B and methylene blue photodegradation.

According to the results obtained, the samples possess absorption in the visible range, with the impregnated titania showing broader peaks without clear signs of surface plasmon resonance. The second series prepared by photoreduction, however, does demonstrate defined SPR peaks in the range of 480-525 nm, depending on the amount of Ag. The TPR-$H_2$ analysis carried out for the Ag/$TiO_2$-IMP series indicated the reduction of Ag in the range of 110-120°C. It was shown that the highest experimental rate constant in the testing photocatalytic reaction is demonstrated by 1% Ag/$TiO_2$-PR, being twice as more as the rate constant of undoped $TiO_2$ Degussa P25. Generally, photoreduction method was shown to be superior to impregnation method for amounts of Ag less than 3% wt. during the course of RhB photodegradation experiment. However, it should be noted that the influence of Ag content on the rate constant is varied in different preparation methods. Moreover, the discussed samples showed photodegradation of methylene blue with notably different results, where the content of Ag in the system did not change the reaction rate completely. This effect might be attributed to silver leaching from the system due to the presence of sulfur-containing methylene blue degradation intermediates.

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# Bifunctional catalysts for vegetable oil hydrotreatment into isomerized alkanes

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The increasing of motor fuels consumption, reducing production of light low-sulfur crude oils, as well as environmental problems is giving rise to seeking fossil energy sources replacement [1]. Vegetable oil cannot be used as a fuel for modern engines but they are of great interest as a feedstock for further processing into the components of fuels. Thus, today there is a great interest to development of approaches to the processing of vegetable oils as well as microalgae lipids into fuels similar to conventional diesel and jet fuels using hydrotreating processes and hydroisomerization.

Catalytic vegetable oil hydrotreating (hydrodeoxygenation, hydrodecarboxylation, hydrodecarbonylation) is pivotal because it allows the conversion of fatty acid triglycerides into normal alkanes and significantly reduces the oxygen amounts. Traditionally, for the hydrotreating noble metal based catalytic systems and petroleum hydrotreatment sulfided catalysts (Co-Mo, Ni-Mo) are usually used [2]. To date, the development of inexpensive stable catalysts for hydrotreating (HDO) of fatty acid triglycerides into fuel normal alkanes, which do not require their sulfidation, is extensively sought. Nickel-based catalysts, along with low cost, show a relatively high activity in HDO [3]. According to the literature, the modification of such catalysts with various metals (Cu, Mo, etc.) [4] and phosphorus may contribute to changes in their activity in various processes but increase stability instead.

The subsequent stage of catalytic isomerization of normal alkanes produced at the hydrotreating (HT) stage, allows obtaining more components of traditional motor fuels, i.e. isoalkanes. The reaction of hydroisomerization (HI) of n-alkanes is carried out in the presence of bifunctional catalysts containing metallic centers for hydrogenation/dehydrogenation and acidic centers for the skeletal isomerization [5]. The HI is always accompanied by hydrocracking, which reduces the yield of targeted isomerized alkanes to some extent and leads to the formation of the lighter and less valuable products. The selectivity to isoalkane formation depends on the balance between activity of the metal for hydrogenation/dehydrogenation processes, as well as the density and strength of acid sites on the support and its textural characteristics.

Nowadays, the consecutive conducting of hydrotreating and isomerization processes in two separated stages is a significant disadvantage, which complicates the processing of vegetable oils and microalgae lipids in the components of motor fuels, giving rise to increased cost and reduced yield of the target products. Thus, bifunctional one-step process catalysts of hydrotreating of the fatty acids triglycerides should have non-sulfided nature, low cost, high activity to deoxygenation and selectivity to iso-alkanes of fuel purposes in comparison with the cracking products.

A series of nickel-based catalysts modified by various metals (Mo, Cu, W) and phosphorus was synthesized by impregnation approach. Alumina, silica and ZSM-5 was used as a support. Catalysts were investigated by a wide range of physical and chemical methods (XRD, XPS, TPR, etc.). It was shown that catalysts modification by Cu, Mo and W could significantly change selectivity as well as yield of the product.

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# Air conditioning system on the plane

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Ozone in the Russian Federation belongs to the first class of hazard of harmful substances [1]. In accordance with the requirement of Circular No. РЦ 25.832-1 for aircraft air environment the following values of the maximum permissible ozone concentration were adopted:

- MPK1 = 0.25 ppmv at any time with a flight altitude of more than 9750 m.

- MPK2 = 0.1 ppmv is the weighted average ozone concentration for a flight that lasts more than 3 hours with a flight altitude of more than 8250 m.

To maintain the required ozone concentrations on aircraft, a number of technical solutions are used, one of which is the ozone converter. The ozone converter is part of the catalytic air conditioning system.

An important part of the ozone converter is a cartridge with a catalyst, which is formed from a carrier and an impregnating solution. The impregnating solution is used as an aqueous alcohol solution of a transition metal (for example, Mn) with the addition of noble metal nitrates, silver or ruthenium. The main problem is the choice of carrier for the catalyst. The carrier should combine heat resistance and mechanical strength, etc., and also a high degree of ozone decomposition after impregnation of the impregnating sol.

According to our research and review of patent literature, there are several companies producing ozone converters: BASF Catalysts, Liebherr-Aerospace Toulouse SAS, Semler Industries, Honeywell, LIMCO Airepair, Saywell International [2, 3, 4, 5].

The production of ozone converters on the territory of the Russian Federation is currently unavailable, so the development of this product is relevant to the provision of civil aviation aircraft.

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# Fe(III), Co(III) and Cu (II) hydroxides supported on zeolite matrices as effective catalysts for water oxidation to dioxygen by $Ru(bpy)_3^{3+}$

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The process of artificial photosynthesis is the one of the most interesting alternative energy source because it provides the direct conversion of solar energy into energy of chemical bonds. The significant obstacle for its implementation is the water oxidation reaction (WOR), which required the simultaneous transfer of four electrons from two water molecules [1]. In order to overcome these difficulties it is reasonable to use catalytic systems that mimic the action of oxygen evolving complex of natural photosystem II [2]. From this point of view, the catalyst must satisfy a number of requirements: First, the catalyst active center must have a hydroxide nature and contain atoms of transition metals capable of taking three consecutive oxidation states (e.g. Mn, Fe and Co it is II, III and IV oxidative states, and I, II and III for Cu). Besides this, the stabilizing support should not be strong electron donor or acceptor to avoid changing of catalyst oxidative potential [3].

Here we synthesized an effective bioinspired catalysts supported onto zeolites based on oxides/hydroxides of Fe(III), Co(III) and Cu(II). We prepared the catalysts by three various techniques: the ionic exchange of H-form of zeolite with aqueous solutions of corresponding metal salt; the wetness impregnation of H-form of zeolite with aqueous solutions of corresponding metal salt; the polycondensation with ammonia of catalytically active component in zeolite channels. We studied the influence of support structure, texture and acidic properties on catalysts efficiency. We characterized obtained catalysts with UV-DRS, TPR $H_2$ EPR spectroscopy and tested them in WOR:

$4Ru(bpy)_3^{3+} + 2H_2O \rightarrow 4Ru(bpy)_3^{2+} + 4H^+ + O_2\uparrow$, (bpy=2,2'-bipyridine).

The use of zeolite supports allowed us to fine-tune the state of active site. We found that ZSM-5 zeolite in compare with BEA, MOR and Y provided formation of most selective catalysts due to smallest channels (5 Å). The catalysts contained active component in hydroxide form represented higher efficiency than that of oxide one. We found that maximum efficiency achieved over catalysts, which had active site in state of hydroxide clusters stabilized inside zeolite channels. The highest $O_2$ formation selectivity obtained in presence of such catalysts were 74; 78; 64 % at pH 10.0 for Co-, Fe- and Cu-contained ones, respectively. Testing of these catalysts in WOR varying catalyst concentration revealed the same dependencies with colloidal hydroxide catalysts. The [catalyst]/[$Ru(bpy)_3^{3+}$] ratio strongly affected catalysts selectivity. The change of pH did not significantly affect the $O_2$ yields (70; 73; 60 % $O_2$ at pH 9.2) due to strong stabilization of hydroxide nanoclusters in zeolite channels. In presence of phosphate buffer, we observed the formation of metal-phosphates, which were less active in WOR. We tested Fe/ZSM-5 in phosphate and borate buffers with pH 8.0, the $O_2$ yields were 13 and 56 % $O_2$, respectively. We test Co-catalyst in five consecutive reuse cycles. The $O_2$ yields was 64 / 63 / 61 / 60 / 60 %. Thus, the use of ZSM-5 zeolite resulted in strong stabilization of active clusters in zeolite channels, significantly reduced the effect of pH, and provided a high stability of catalysts with a TON more than 1.8.

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# Hydrogenolysis of lignine in supercritical ethanol. The influence of nature of catalyst active sites and reducing agent

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Lignin depolymerization into lignin monomers has fascinated researchers for decades as a pathway to valorize lignin biopolymer [1]. However, there are a number of obstacles that need to be overcome before lignin processing becomes economically viable [2]. Here, we report the study of the catalytic hydrogenolysis of grass, soft and hard wood lignins (corncob and birch wood ethanol-lignin [3], pine wood hydrolytic lignin) in the supercritical ethanol over solid bifunctional catalysts, which contain acidic and metallic sites. The hydrogenolysis process was conducted at 260 ºC and 60-80 bar during 6 hours. The products of reaction were studied using GC-MS and GC.

The influence of catalyst support nature was studied using three different acid-basic materials, namely: sepiolite, zeolite ZSM-5 supported on $Al_2O_3$ and Sibunit (Sib) graphite-like carbon promoted via oxidation. The Sib material was found to produce highest yield of liquid products due to the highest amount of surface acid sites [4]. The increase of acid sites concentration of Sib led to formation of bigger amount of ethanolysis products resulted from lignin depolymerization. The bifunctional Ni- and Ru-containing catalysts based on oxidized Sib support were prepared and characterized [5]. Applying metal-containing Sib catalyst in lignin depolymerization process allowed us to decrease the coke formation and to increase the amount of aromatic monomers and the total yield of liquid products up to 81 % (36 % were monomeric components) in case of 3% Ru/Sib catalyst. According to GC-MS, the use of Ni-contained catalysts provided formation of C-C bond cracking products of alkyl fragments of lignin. The increase of Ni content led to a decrease in the amount of cracking products of the aliphatic substituent and to increase in the yields of the hydrogenolysis products (total yield of liquid products was 72 %, the monomeric products content was 25 %). The result obtained over 3% Ni/Sib catalyst was inferior to the result obtained in presence of 1% Ru/Sib catalyst. The use of Ru-contained catalysts led to the formation of deoxygenation products. The increase of Ru content resulted in intensification of hydrogenation processes. We found that reducing agents significantly affected process: using $H_2$ / i-PrOH / HCOOH led to increasing of liquid phase content up to 89 % (39 % is monomeric components) and decrease coke formation (less than 4 %). Moreover, the choice of reducing agent changed main product components distribution: in case of $H_2$ and i-PrOH it was 4-propilsyringol, when HCOOH used it was 4-allylsyringol. The origin of lignin (biomass nature and separation technique) significantly affected depolymerization process. Well soluble ethanol-lignins provided high yields of liquid products (70-90 %). Nevertheless, ethanol-lignin obtained from corncob biomass provided low monomeric products yield (15 %). The hydrolytic lignin of pinewood provided high char formation. The liquid products took only 52 % (36,5 % was monomeric products). Aromatic monomers (p-allylsyringol, p-propyl syringol, p-propylgivacol, etc.) obtained in catalytic hydrogenolysis process of lignin are valuable raw materials for the chemical and pharmaceutical industries, and also can be used for the production of polymers and fuel additives.

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# Development of bifunctional catalysts based on Ru supported on CsHPA for hydrolysis-hydrogenolysis of cellulose to ethyleneglycol and propyleneglycol

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Ethylene and propylene glycols (EG and PG) are widely used in industry to produce antyfreezes and other valuable chemical products [1]. PG is a non-toxic substance, therefore it is used in pharmaceutical, food, industries. EG and PG are traditionally produced from non-renewable recourses. Constant depletion of traditional raw materials and negative impact of their utilization onto environment course the interest to plant biomass as an alternative renewable resource. One-pot hydrolysis-hydrogenolysis of inedible cellulose which is a polysaccharide component of lignocellulose biomass seems to be a promising and effective method to form EG and PG.

Two sequential catalytic steps (hydrolysis and hydrogenolysis) must be applied to obtain EG and PG from cellulose. Acid catalyst must be used for hydrolysis of polysaccharide to get glucose. Heteropoly acids (HPAs) and cesium salts of HPA (CsHPAs) have acidic centers and that is why they are considered as perspective acid solid supports. Hydrogenolysis of glucose to EG and PG proceeds over noble metal nanoparticls (ruthenium, for example) [2]. Thus, the aim of the study was the development of bifunctional catalysts of Ru/CsHPA, Ru/HPA/$ZrO_2$ and Ru/HPA/$Nb_2O_5$ having acidic and reductive centers which seems to be very perspective for the EG and PG production via one-pot hydrolysis-hydrogenolysis of cellulose under harsh conditions.

Ru/CsHPA, Ru/HPA/$ZrO_2$ and Ru/HPA/$Nb_2O_5$ (where CsHPAs was $Cs_3HSiW_{12}O_{40}$; $ZrO_2$ and HPA/$ZrO_2$ and HPA/$Nb_2O_5$ are $Nb_2O_5$ and $ZrO_2$ covered by $H_3PW_{12}O_{40}$ and calcinated under the air at 550 °C) were prepared via impregnation the support by Ru precursor $Ru(NO)(NO_3)_3$. The catalysts were investigated by IR spectroscopy, $N_2$ absorption, XRD, AES-ICP, TEM (for Ru-containing samples only) and were tested in the one-pot hydrolysis-hydrogenolysis of mechanically activated crystalline cellulose. The reaction was performed in the autoclave at 245 °C under $H_2$ (5 MPa). The concentrations of products were measured by HPLC. Total organic carbon content was also controlled.

According to ICP-AES, the solubility of Zr, Nb, W, Cs, Si is low, that indicates the stability of the catalytic systems. According to received $N_2$ absorption data, the diameter of catalyst micropores is increased after the application of Ru on HPA/$ZrO_2$, HPA/$Nb_2O_5$.IR spectroscopy and XRD of Ru-containing catalysts show no changes of support structures during the precipitation of Ru on CsHPAs, HPA/$ZrO_2$, HPA/$Nb_2O_5$. TEM analysis of Ru-containing catalysts shows that ruthenium nanoparticles have average size equal from 1.1 to 1.5 nm.

The one-pot hydrolytic hydrogenation experiments have been performed with all the catalysts and there pure supports without ruthenium to reveal the importance of acid and metal catalytic centers in the reaction under investigation. CsHPA, HPA/$ZrO_2$, HPA/$Nb_2O_5$ tested separately do not show activity in hydrolysis-hydrogenolysis of cellulose. Addition of Ru causes EG and PG formation with yields up to 26 % and selectivity up to 72 %. Catalysts of Ru/CsHPA were active in the reaction whereas Ru/HPA/$ZrO_2$ and Ru/HPA/$Nb_2O_5$ showed low activity (yields EG and PG were 0.7-2 %). The highest yields of EG and PG equal to 26 and 11%, respectively, were achieved in the presence of 1% Ru/$Cs_3HSiW_{12}O_{40}$ catalyst.

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# Direct catalytic oxidation of $H_2S$ to sulfur

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More than 40 % or > $70•10^{12}$ $nm^3$ of the world's hydrocarbon gas reserves are hydrogen sulfide containing natural and oil-associated gases [1]. This feedstock is a significant potential resource for energetics and chemical synthesis. However, high content of hydrogen sulfide (1-30 vol.%) excludes the direct application of these gases as fuels or raw materials for downstream production. The currently used flame combustion of such gases leads to air pollution with toxic sulfur di- and trioxide, sulfuric acid, products of incomplete combustion of hydrocarbons, and carcinogenic soot, amount of which attains one million tons a year. Thus, the development of technical solutions for reliable on-site purification of these gases is a problem of the highest priority for the Russian Federation and the whole world.

In the Laboratory of Environmental Catalysis of the Boreskov Institute of Catalysis, new processes based on direct catalytic oxidation of hydrogen sulfide were developed. Main advantages of this method are: a single catalytic reactor providing $H_2S$ conversion of up to 99 %, mild reaction conditions (T=220-280 °C), selective oxidation of $H_2S$ in the presence of hydrocarbons and possibility to build and operate units of small and medium size [2, 3].

Two versions of the technology have been developed: in the reactor with a fluidized bed of catalyst and in the reactor with honeycomb monolithic catalyst. Nowadays this technology was successfully tested in the pilot and industrial scale on the largest sour gas fields, refineries and gas processing plants in Russia, such as Astrakhan and Orenburg sour gas fields and Ufa refineries [3-7].

The efficiency of hydrogen sulfide removal was proved to exceed 99%.

During two years of continuous operation:

650 million $m^3$ of commercial gas were produced;

3500 tons of hydrogen sulfide were recovered as elemental sulfur;

emission of more than 7000 tons of sulfur dioxide and sulfuric acid to the atmosphere was prevented;

pollution damage for the amount of $15 million was averted.

The technologies for purification hydrocarbon feedstock based on direct selective oxidation of hydrogen sulfide have been developed. The efficiency of the technology has been proved upon field testing of industrial installations. Characteristics of the produced sulfur surpass those specified by Russian National Standard #127.1-93 (commercial grade sulfur 9990).

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# Multifunctional catalysts for one-stage hydrothermal upgrading of biomass with *in situ* hydrogen production

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Plant biomass as a source for fuel production is the most promising alternative to fossil resources. However, the processes being developed to convert biomass into liquid fuels are still uncompetitive, compared to traditional processing of fossil feedstocks.

Currently, the process of obtaining biofuels from plant raw materials through biomass liquefaction is carried out in several stages: 1) bio-oil production via rapid pyrolysis or hydrothermal liquefaction; 2) hydrogen production; 3) catalytic hydrodeoxygenation / hydrocracking of bio-oil to obtain fuel components with low oxygen content (less than 10 wt. %). The disadvantage of this approach is the complexity due to the multistageness and the need in hydrogen produced separately, as well as the low quality of the bio-oil.

Pyrolysis and hydrothermal liquefaction (HTL) of biomass are two approaches allowing to obtain similar in composition intermediate liquid products (bio-oil). The main difference between pyrolysis and HTL is the need to carry out the pre-drying stage of raw materials. In addition, products obtained from using HTL process of plant biomass have a lower oxygen and water content, and also have a higher value of calorific value compared to products obtained as a result of pyrolysis. One of the most used type of plant raw materials processing by HTL is a wood raw material (lignocellulosic biomass) [1]. Unfortunately, the obtained bio-oil cannot be directly used as a fuel. Further processing of bio-oil is required to increase its stability and quality, due to the high content of oxygen-containing and high-molecular compounds in its composition. Catalysts used in the bio-oil hydrotreatment processes must be active in catalytic cracking and hydrodeoxygenation.

Glycerol aqueous-phase reforming for hydrogen production is a relatively new approach to obtain energy from plant biomass [2]. Currently, there is a steady increase in the production of biodiesel and, as a consequence, glycerol as the main by-product [3]. The aqueous-phase reforming is carried out at lower temperatures than steam reforming (470 – 535 K) and at elevated pressure (of 1.5 – 5.0 MPa) [4].

This work is aimed at the development of refined bio-oil production from plant biomass by its liquefaction in hydrothermal conditions in one stage. Glycerol being a multi-tonnage byproduct, formed in the production of biodiesel acts as a hydrogen source. Thus, this process combines in the same reactor in one stage three catalytic processes, which are usually carried out sequentially in three stages: bio-oil production through biomass liquefaction, hydrogen production and hydrotreatment of bio-oil. Such a merger would lead to improved process energy efficiency and lower capital and operating costs.

A series of nickel-based catalysts modified by various metals (Mo, Cu) was synthesized. Catalysts were investigated by a wide range of physical and chemical methods. A correlation was established between the activity of catalysts in aqua-phase reforming of glycerol and one-pot process of guaiacol conversion using glycerol as a source of hydrogen and their physical and chemical properties.

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# Development bifunctional Ru-containing catalysts for one-pot hydrolysis-hydrogenation of cellulose to sorbitol

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Sorbitol is a compound which is widely used in pharmaceutics and food ndustry as a sweetener. Sorbitol is currently produced from starch and sucrose via biotechnical or catalytic methods. Another perspective way of obtaining this polyol is the one-pot hydrolysis-hydrogenation of inedible cellulose. Cellulose is a main polysaccharide component of renewable lignocellulose biomass (up to 70 %). Utilization of inedible cellulose as a source for sorbitol production eliminates a competition between food and industrial applications of polysaccharide resources (starch and sucrose).

Sorbitol can be obtained from cellulose in two sequential catalytic stages (hydrolysis of polysaccharide and reduction of glucose). Insoluble hot water $ZrO_2$ and $Nb_2O_5$ oxides are efficiently able to catalyze hydrolysis of polysaccharide to glucose. Heteropoly acids (HPAs) have acidic centers and also to be perspective acid catalyst. Combination of acidic oxides and HPAs let one to develop a perspective solid acid catalyst of hydrolysis. Ruthenium nanoparticles are one of the most promising catalytic systems for the reduction of glucose to sorbitol. Thus, the development of bifunctional catalysts as Ru/HPA-$ZrO_2$ and Ru/HPA-$Nb_2O_5$ having acidic and reductive centers seems to be very perspective for the sorbitol production via one-pot hydrolysis-hydrogenation of cellulose under hydrothermal conditions.

The purposes of the study were the development of the bifunctional ruthenium catalysts supported on the oxides of niobium or zirconium covered by heteropoly acids (Ru/HPA-$ZrO_2$ and Ru/HPA-$Nb_2O_5$) and testing the catalysts developed in the one-pot conversion of cellulose to sorbitol.

The HPA-$ZrO_2$ and HPA-$Nb_2O_5$ were synthesized by the precipitation of $H_3PW_{12}O_{40}\times xH2O$ on $ZrO_2$ and $Nb_2O_5$, which were made from $ZrOCl_2\cdot 8H_2O$ and $NbCl_5$, respectively. The obtained supports were annealed under the air at 450, 550 and 650 °C to calcine HPA. Further, 3.0% of Ru was precipitated on HPA-$ZrO_2$ and HPA-$Nb_2O_5$ supports from an aqueous solution of $RuCl_3$ and reduced at 250 °C to form metal nanoparticles. The catalysts were characterized by IR spectroscopy, $N_2$ absorption, AES-ICP, XRD, TEM. Supports and Ru-containing catalysts were tested in the one-pot hydrolysis-hydrogenation of mechanically activated crystalline cellulose at 180 °C under $H_2$ (5 MPa). Concentrations of products were measured by HPLC. Total organic carbon content was also controlled.

Structures HPA-$ZrO_2$ and HPA-$Nb_2O_5$ were stable during precipitation of Ru. The solubility of all supports is low, that indicates the stability of the catalytic systems. According to received $N_2$ absorption data, the specific surface area and microporous volume is decreased, but the diameter micropores of catalyst is increased after the application of Ru on both HPA-$ZrO_2$ and HPA-$Nb_2O_5$. The average particle size of Ru was in the range of 0.7 to 1.4 nm.

HPA-$ZrO_2$, HPA-$Nb_2O_5$ supports are not active in the hydrolysis-hydrogenation of cellulose and, on the contrary, demonstrated moderate activity in hydrolysis reaction. Introduction of Ru to the catalytic systems made the sorbitol formation possible (the yields of goal product were equal to 18-49 % (selectivity up to 85 %)). By-products (mannitol and glucose) with yields up 8% were also detected over Ru/HPA-$ZrO_2$ and Ru/HPA-$Nb_2O_5$. Bifunctional Ru/HPA-$ZrO_2$ catalysts show a higher catalytic activity compared to Ru/HPA-$Nb_2O_5$ systems. The conversion of cellulose and yields of sorbitol increased with increasing the calcination temperature of the supports (HPA-$ZrO_2$ and HPA-$Nb_2O_5$) from 450 to 550 ° C, but decreased with increasing temperature to 650 °C. The highest yield of sorbitol equal to 49% was achieved in the presence of 3% Ru/HPA-$ZrO_2$ (550 °) catalyst.

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# MgAl and LiAl mixed oxides as efficient catalysts for aqueous Claisen-Schmidt condensation of biomass-derived furfural with ketones

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Furfural produced from plant biomass is the precursor to a wide range of furan-based chemicals such as 2-methylfuran, tetrahydrofuran, furfuryl alcohol, tetrahydrofurfuryl alcohol, etc. Claisen-Schmidt condensation of furfural with ketones allows obtaining a variety of valuable furfurylidene ketone-based compounds. Recently, there is a challenge to develop heterogeneous catalysts, which are highly active, economical and eco-friendly in the above-mentioned reaction [1, 2].

We studied the effect of composition and physicochemical properties of MgAl and LiAl mixed oxides on their catalytic properties in the aqueous Claisen-Schmidt condensation of furfural with acetone and cyclohexanone. It was shown that $MgAlO_x$ and $LiAlO_x$ catalysts are highly active in furfural conversion. The most basic $LiAlO_x$ catalyst with the Li/Al atomic ratio of 0.5 provides a high rate of the reaction between furfural and acetone. The MgAl oxide catalysts are less active in the same reaction, but allow achieving a high selectivity to furfurylidene acetone (97 %) at almost complete conversion of furfural. Moreover, the $MgAlO_x$ catalysts were shown to be highly active in the condensation of furfural with cyclohexanone. The sample with the Mg/Al atomic ratio of 4 allows achieving a 90 % conversion of furfural giving furfurylidene cyclohexanone in a high yield.

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# Influence of the method for obtaining active alumina on the physicochemical properties of the catalyst in the dehydration of 1-phenylethanol to styrene

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Styrene is one of the most important monomers of polymer chemistry which is often used with other comonomers in the production of synthetic rubbers, resins and plastics to improve mechanical strength, heat and chemical resistance, dielectric and other properties of the finished material. A vapor-phase process for the dehydration of 1-benzeneethanol into styrene is widely used in the industry, where active alumina is used as the catalyst. The alumina properties are determined by the characteristics of its aluminum hydroxide precursor pseudoboehmite structure.

Pseudoboehmite is currently carried out in a variety of ways, but the most common method is the acid reprecipitation of alumina. An important advantage of the method is the possibility of obtaining various aluminum hydroxides depending on the conditions (temperature, pH, precipitation and stabilization time) as well as controlling the phase composition of precipitation and the phase ratio. In the present study, precipitation of aluminum hydroxide was carried out from aluminum nitrate with an aqueous solution of ammonia in the pH range 6-9 at temperatures of 50-100 °C using continuous sedimintation technology. In addition to the basic product, pseudoboehmite, depending on the reaction conditions, the formation of X-ray amorphous aluminum compounds in an amount up to 40 wt.% is noted.

At the moment, the effect of X-ray amorphous aluminum compounds inevitably formed as a result of pseudoboehmite production on the properties of the porous system and the acidity of the oxide surface has not been studied enough. Therefore, it is important to study the effect of X-ray amorphous compounds in the pseudoboehmite composition on the porous hydroxide system and the acidity of the oxide surface which is used as a catalyst for the acid catalyzed dehydrogenation of 1-benzeneethanol in styrene.

Alumina catalysts have been investigated, the precursor of which has up to 40 wt.% of X-ray amorphous aluminum compounds. The catalysts were obtained at 550 and 750 °C. The X-ray amorphous phase forms amorphous alumina at 550 °C. The amorphous alumina transforms to $\gamma$-$Al_2O_3$ at 750 °C. The acidity of the oxide surface and a maximum on the differential curve for the pore volume distribution over the diameters decreases with an increase in the calcination temperature from 399 to 302 μmol/g and 11 to 7 nm consequently. At the same time, the activity and yield of styrene increase by 4 % and selectivity increases too of 10 % in the reaction of vapor-phase dehydration of 1-benzeneethanol.

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# Influence of steam addition on matrix conversion of methane to syngas

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One of the effective methods of syngas production may be matrix conversion of natural gas. Partial oxidation of the gas in the matrix conversion takes place in the gas phase near the inner surface of the matrix, made of permeable for gas and heat-resistant material. The surface of the matrix stabilizes the flame front above it. Therefore, in terms of matrix conversion, it is possible to burn fuel-rich mixtures, the conversion of which is impossible under normal conditions. Earlier successful tests of methane matrix conversion using air oxygen and technical oxygen as oxidizing agents have been carried out, which showed high efficiency of converters of this type [1-3]. However, when using air oxygen, the resulting synthesis gas was strongly diluted with nitrogen, which makes it difficult to use it in further catalytic processes. Synthesis gas with a low nitrogen content was obtained during the transition from air oxygen to technical oxygen. But when using technical oxygen, the temperature of conversion was extremely sensitive by changes of the input parameters. Stabilization of the conversion was achieved by adding water vapor to the initial mixture, which allowed to increase the specific productivity of the Converter for methane by 30%. However, the contribution of reactions involving water at a conversion temperature of ~ 1000-1100 0C was insignificant, so the addition of water vapor does not solve the problem of low process rates. Thus, the maximum achieved process indicators are: $H_2$ content in dry synthesis gas up to 56 % (vol.), CO – 32 % (vol.) ($H_2$/CO ratio= 1.8), total hydrocarbon content of $C_{2+}$ up to 2 % (vol.), $CO_2$ up to 7 % (vol.), $CH_4$ conversion up to 85 %.

It is known that one of the industrial methods of synthesis gas production is steam conversion of methane. Therefore, it is possible to increase the indicators of this process by including the catalytic stage of steam hydrocarbons conversion. Steam hydrocarbons conversion are diluted hydrogen and carbon monoxide is currently being investigated at the laboratory with the use of catalysts developed by GIAP.

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# Catalytic properties of $Sr_{2-x}La_xTiO_4$ oxides (x = 0-2) in oxidative coupling of methane

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Currently, methane is industrially converted through catalytic steam or autothermal reforming to synthesis gas, i.e. a mixture of CO and $H_2$. The oxidative coupling of methane (OCM) is one of the promising ways of obtaining ethane and ethylene directly from natural gas, excluding the stage of synthesis gas production [1, 2]. However, the process currently has no practical realization. The reason is primarily due to the low activity and selectivity of the used catalysts. Among the recently tested catalysts, $SrTiO_4$ was shown to be very active for the oxidative methane coupling [3], and its activity was found to further improve when Sr was partially substituted by La.

The goal of this study is investigation of effect of the Sr substitution degree on the physicochemical and catalytic properties of $Sr_{2-x}La_xTiO_4$ oxide catalysts in the oxidative coupling of methane.

The catalysts were prepared by precipitation of $Sr(NO_3)_2$ with a $K_2CO_3$ from an aqueous solution in the presence of a $TiO_2$ suspension. The following composition were prepared: $Sr_{2-x}La_xTiO_4$, $x \in [0, 2]$, the step = 0.2. The samples were characterized by physicochemical methods.

The catalytic activity was measured in a fixed-bed quartz tube reactor (5 mm i.d.) at 800–900°C and ambient pressure. The temperature of the catalyst was measured with chromel–alumel thermocouple adjusting the outer surface of the reactor at the middle of the catalyst bed. Gas mixture consisted of $CH_4$, $O_2$ and $N_2$ was introduced in the reactor using flow mass controllers. Reactant and product concentrations were analyzed by *on-line* gas chromatograph. The reaction products were ethane, ethylene, water, CO, hydrogen and $CO_2$. A blank run (quartz tube filled with only inert $SiO_2$ particles of 0.25–0.5 mm in size) showed no conversion at the reaction conditions.

XRD analysis showed that the sample of $Sr_2TiO_4$ has well-crystallized structure similar to a ‘layered’ perovskite without admixtures of another phases. In the structure of the samples with substitution degrees from x = 0.2 to 0.6, in addition to the main phase of $Sr_2TiO_4$, an insignificant amounts (admixtures) of the $TiO_2$ phase (rutile) and $La_2O_3$ phase were revealed as well. An increase in the stoichiometric content of La leads to the stratification of the $Sr_2TiO_4$ main phase with the structure of a ‘layered’ perovskite and the formation of a perovskite phase $SrTiO_3$. The $SrTiO_3$ perovskite and the $La_2O_3$ oxide become the main phases in samples with x = 1-1.2. In the region of high substitution degree ($x > 1.4$) a separate phase of lanthanum oxycarbonate $La_2O_2(CO_3)$ is detected, which is due to the ability of $La_2O_3$ to easy adsorb of $CO_2$ and interact with it.

The prepared substituted titanates $Sr_{2-x}La_xTiO_4$ were tested in the OCM reaction under the following conditions: $CH_4$ mixture composition is $CH_4/O_2/N_2=45/11.3/43.7$, temperature is 800°C, pressure is 1 bar. It was shown that the samples with La content (x) in the range of 0.8-1.8 demonstrated the higher activity in the series. This may be due to the presence of $La_2O_3$ phase with an optimal crystallites size and a possible admixture of poorly crystallized SrO.

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# Catalysts of block form with spherical aggregates of composition $TiO_2$-$Cr_2O_3$ in the oxidation of p-xylene

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Catalysts containing chromium oxygen compounds as an active component are of great industrial importance and are widely used in petroleum gas processing processes [1]. As a result, the development of a new type of catalyst is of particular interest for the industrial processing of hydrocarbons.

In the presented work, we investigated spherical $TiO_2$-$Cr_2O_3$ materials in the block $SiO_2$. The method of preparation consisted of several stages. The first one was the preparation of the spherical substrate by sorption of $Cr_2O_7^{2-}$ ions by polymer material from aqueous solutions. The second stage was the preparation of aggregately stable sols on the basis of tetrabutoxytitane, water, and nitric acid, and deposition of sol particles on the spherical substrate during 12 hours. Then, the spherical material was dried at 70 °C for 60 min. The spherical aggregates are mixed with a liquid $SiO_2$ and placed in a quartz tube. The obtained block composites were stepwise calcined to a temperature of 800 °C.

The spatial structure of the spherical material was studied by digital 3D-microtomography (Russia) [2].

The catalytic activity of the $SiO_2$-$TiO_2$-$Cr_2O_3$ samples was measured in the model reaction of p-xylene oxidation. The reaction was performed in a flow catalytic setup using quartz tube reactor with an inner diameter of 8 mm, a feed rate of 29.7 L/h. Qualitative and quantitative analysis of the starting mixture and the products of the oxidation of p-xylene were performed on «Simex» FT-801 spectrometer.

The results of 3D microtomography showed that obtained block materials have cavities in which spherical aggregates $TiO_2$-$Cr_2O_3$ are located. Spherical aggregates have a layered structure. The inner layer of the oxide part of the spherical sample is represented by $Cr_2O_3$ and the outer layer by the oxide layer of $TiO_2$.

Oxidation of p-xylene on $SiO_2$-$TiO_2$-$Cr_2O_3$ sample started at 175 °C. Selectivity of $SiO_2$-$TiO_2$-$Cr_2O_3$ toward products of deep oxidation was 100 %. In the temperature range 200-300 °C, the emission of carbon monoxide is observed. The degree of conversion of p-xylene reached 100 % at 450 °C.

The block materials $SiO_2$-$TiO_2$-$Cr_2O_3$ sample was active in the reaction of deep oxidation of p-xylene.

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# Tests of samples of filtering-sorbing materials with introduced photocatalyst

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Photocatalytic purification is a subject of scientific and commercial interest of a large number of researchers.

The purpose of the tests was to quantify the change in the vapor concentration of acetone, ethyl acetate, benzene, xylene and ammonia in a sealed chamber during photocatalytic purification using a filter-sorbing material (FSM) with the introduced photocatalyst.

For the tests, FSM samples were produced by applying a catalytic composition containing titanium dioxide to the fabric base. Samples differed in the composition of the tissue and the mass fraction of titanium dioxide on the fabric.

To develop a methodology for using FSM in protective products and life support systems, it is important to define how the current concentration of harmful impurities in an isolated volume will change. A sealed chamber with a volume of 150 $dm^3$ was chosen as the main element of the sample testing facility.

The installation included a fan for mixing the gas-air composite while dosing impurities, a moisture and temperature meter, an inhaler of an inhalator type, a heat exchanger with a coolant. The evaluation of the catalytic activity was carried out at an incident radiation power of 10-20 $mW/cm^2$. For testing, a lamp of 300 mm in length and 15 W was selected. Samples 330 mm long were attached around the lamp on aluminum rigid rings without being connected to the edges of the fabric. The content of harmful impurities was estimated on a gas chromatograph "Kristall 2000M" and on a multicomponent gas analyzer.

During the tests, prior to dosing each harmful additive, luminous rehabilitation of the samples was carried out with the lamp on for three hours.

The analysis of the results obtained in the course of the tests showed that in all cases of application of the materials studied, air purification from harmful impurities occurred. The most effective cleaning was obtained from ethyl acetate, ammonia, m-xylene. Less efficient was the removal of benzene and acetone.

It was found out that the most catalytic activity was a sample containing 4.14 % of mass titanium dioxide applied to a 100 % cotton material.

# Structured catalysts for hydrocarbon oxidation processes

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The development of highly efficient modular power generation units is of great importance. Solid oxide fuel cells (SOFC) are currently considered as the most efficient devices for the conversion of hydrocarbons (natural gas, LPG, JP or diesel) into electric power. To provide stable SOFC operation, initial fuel, before feeding to the SOFC anode, should be converted to synthesis gas with high hydrogen content [1]. Catalytic steam (SR), combined steam-dry (SDR), partial oxidation (PO) or autothermal reforming (ATR) are the most appropriate reactions for this purpose. The optimum temperature for these reactions is 550 − 900 °C, which falls within the SOFC working temperature range. Diesel fuel is a promising substance for conversion into hydrogen-rich gas for SOFC feeding due to readily available infrastructure and wide application scope. As shown in a number of works [2,3], noble-based catalysts demonstrate high activity and selectivity for hydrogen-rich gas production both in lab scale and short term pilot scale experiments. Also, most studies are considering catalysts in the form of a powder. In this work the catalyst performance, using engineered substrates in the form of FeCrAl metal meshes and blocks, was studied for real-life applications under real reaction conditions.

The catalysts supported on structured carriers (FeCrAl blocks) provide controlled reaction conditions throughout the reactor volume that favorably competes, for example, fixed bed reactors. The use of the structured catalysts provides efficient heat and mass transfer, decreased gas dynamic resistance, improved catalyst performance that allows reducing the catalyst quantity per unit volume of the reactor. The opportunity to perform the process under controlled optimum conditions allows to increase the selectivity and minimize undesirable side reactions, such as coke formation.

In this work we studied noble metal (Rh, Pt, Ru) based catalysts for ATR and SR of n-hexadecane and Euro-5 diesel fuel. The catalysts of composition 0.1 mmol/ Rh-, Pt-, Ru/$Ce_{0.75}Zr_{0.25}O_{2-\delta}$, prepared by sorption-hydrolytic deposition technique, demonstrated high dispersity with a particle size of 1-2 nm [4]. Among the catalysts tested in n-hexadecane SR under the the following operating conditions: $H_2O/C = 3$, GHSV = 23,000 $h^{-1}$, T = 550 °C, the Rh-based sample showed the best activity - it provided complete conversion of the fuel during 8 h on stream and the outlet concentrations of $H_2$, $CO_2$, CO and $CH_4$ close to the equilibrium values (54, 18, 5 and 6 vol.%, respectively). The results obtained were used to develop a structured Rh/$Ce_{0.75}Zr_{0.25}O_{2-\delta}$ catalyst comprised of an active component supported on FeCrAl grid pre-coated with η - $Al_2O_3$ [5]. The obtained 0.24 wt.% Rh/$Ce_{0.75}Zr_{0.25}O_{2-\delta}$/η-$Al_2O_3$/FeCrAl catalyst provided a 100% conversion of n-hexadecane in ATR during 12 h, and hydrogen productivity of $H_2$ ~ 2.5 $kg_{H_2} kg_{cat}^{-1} h^{-1}$ [6].

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# Levulinic acid hydrogenation into γ-valerolactone over bimetallic catalysts

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Lignocellulose displays an enormous potential as a green and renewable carbon resource for biofuels and value-added chemicals [1]. Levulinic acid (LA) prepared from lignocellulose is one of the most promising platform molecules for synthesis of fuel additives, plasticizers, chemical solvents, and pharmaceuticals [2]. Due to the cellulose densely packed structure and poor solubility, catalytic conversion of cellulose directly into LA has yet to achieve a breakthrough [3]. Recently significant efforts were put on development of more efficient methods for cellulose activation. Utilization of liquid ammonia for pretreatment of lignocellulosic biomass allowed, for example, conversion of native cellulose to a highly digestible cellulose allomorph and simultaneously extraction of the lignin fraction for downstream catalytic upgrading [4]. Removing lignin that causes enzymes inhibition increased enzyme accessibility to structural carbohydrates and enhanced cellulose reactivity. Acid-catalyzed hydrolysis of cellulose passing through such intermediates as glucose and 5-hydroxymethylfurfural gives crude LA. The latter can be transformed into γ-valerolactone (GVL) and some other products including 2-methyltetrahydrofuran (2-MTHF), alkyl valerates, 1,4-pentanediol (1,4-PDO) and pyrrolidinones, which can affect LA hydrogenation selectivity. Even for neat LA hydrogenation over several monometallic catalytic systems based on VIII metal group such as Pt oxide, Ni Raney and Ru/C showed noticeable deactivation. The yields of GVL over the above mentioned catalysts were of 87% [5], 94% [6], and 96% [7], respectively.

The main objective of the present work was to study LA hydrogenation over bimetallic catalysts - Pt and Ir doped with rhenium supported on alumina and titania in order to improve catalyst stability.

LA (98%, Acros Organics, Belgium) (25 mL, 0.035 M) was hydrogenated over alumina and titania supported PtRe and IrRe (4%+4%) at 180 °C and 25 bar of $H_2$. The catalysts were prepared by impregnation with metal chloride precursors followed by reduction at the temperature determined by TPR. The catalysts were characterized by TEM, XRD and XPS. GLC analysis of the products was done using BP20 capillary column (60 m/0.25 mm/0.25 μm) (Chromos GC-1000) It was shown that, in contrast to $PtRe/TiO_2$, which exhibited selective pentanoic acid formation (yield 80%), LA hydrogenation over $IrRe/Al_2O_3$ mainly resulted in GVL which was further converted into 2-pentanol, traces of 1-pentanol and 2-MTHF as the major product. Note that 2-MTHF is also of high interest as a valuable component of biofuels, a "green solvent" and a promising platform molecule for various organic syntheses. The identified reaction network of LA conversion over $IrRe/Al_2O_3$ is in line with literature data on LA hydrogenation over nickel-copper catalysts [8]. The yield of 2-MTHF (46% after 1.5 h) was higher than for $Ni\text{-}Cu/Al_2O_3$ (56% after 5 h) at a lower temperature (180 °C vs 250 °C). Other potential side products, such as alpha-angelica lactone, 4-hydroxypentanoic acid, pentanoic acid and 1,4-PDO were not detected.

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# Development of size-controlled Ru/C catalyst for selective levulinic acid hydrogenation into γ-valerolactone

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Levulinic acid (LA) is considered as one of the ten top biobased platform chemicals which can be converted into a wide range of valuable chemical compounds [1]. Various catalysts, supports, and solvents have been investigated for hydrogenation of levulinic acid into gamma-valerolactone (GVL). It was found that ruthenium is the most effective noble metal catalyst for this reaction [2, 3]. GVL is gaining considerable attention as a versatile building block, because it can be used as a fuel additive, solvent for biomass processing, as well as a precursor for production of hydrocarbons, polymers and other valuable chemicals, having thereby a strong potential to reduce consumption of petroleum-derived fossil fuels [4]. Recently it was shown that highly dispersed ruthenium in 5%Ru/activated carbon catalyst prepared by solvent-free microwave-assisted thermolytic method exhibited a superior catalytic performance compared with a less dispersed Ru supported on carbon and metal oxide supports. In the presence of this 5%Ru/AC catalyst GVL was produced with a high yield of > 99% under mild reaction conditions (100°C, 2.0 MPa, LA concentration in water 0.10 g/mL) [5]. Synthesis of metal nanoparticles (NPs) in the presence of surfactants provides a precise control of the particle size, composition, shape and microstructure. This method has been thus exploited for preparation of catalysts. In our earlier works the colloidal method for synthesis of Ru NPs immobilized on a carbon support was successfully developed [6] resulting in high activity in hydrogenation of galactose and arabinose [7, 8]. Note that up to now colloidal Ru/C catalysts have not been applied in LA hydrogenation.

This study aims at development of colloidal Ru/C catalysts with a controllable particle size for selective hydrogenation of LA into GVL to elucidate the optimal ruthenium NPs size.

A series of PVP stabilized colloidal Ru NPs was synthesized by the polyol method using $RuCl_3$·nH2O and ethylene glycol with consecutive immobilization on mesoporous carbon Sibunit. Synthesized Ru/C catalysts were purified from PVP by both chemical washing and thermal treatment. Chemical washing was carried out in water or aqueous solutions of acetic acid. The thermal treatment methods were carried out in air (180 °C) followed by $H_2$ (400 °C) as well as in $H_2$ (400 °C), $N_2$ (500 °C), and air (180 °C). Additionally, Ru on Sibunit catalyst was prepared by a conventional impregnated method. LA (25 mL, 0.035 M) (Acros Organics, Belgium) was hydrogenated at 180oC and 25 bar of $H_2$ in a batch reactor. Screening of the catalysts showed that colloidal catalysts being less active than Ru/C prepared by impregnation, were, however, more selective to GVL. Lower activity can be tentatively explained by blocking of active sites with organic impurities. Activity of the colloidal catalysts depending on the catalyst treatment method yielded 84-90% GVL. The catalysts before and after the reaction were analyzed by TEM, XRD, and N2 physisorption. The optimal ruthenium NPs size was found to be 2-3 nm.

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# Preparation of carbon composite containing $Mo_2C$ by mechanochemical synthesis

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Recently in the world there is an increased consumption of oil refining and petrochemistry products as the lower quality feedstock becomes more abundant, additional challenges arise catalyst deactivation and poisoning. Therefore, one way to face these challenges is to develop catalysts that can better withstand the severe operation conditions prevailing in the hydrotreating of heavier gas oils, e.g. an applying as a catalyst of highly dispersed carbides of transition metals. Molybdenum carbides are considered as the new promising catalysts and have been widely investigated in recent years because of their unique physical properties and electronic structure [1]. Molybdenum carbides have similar catalytic properties to noble metal catalysts in various organic chemical reactions due to their resemblance in electronic structure to them [2,3]. It makes molybdenum carbides to be a promising substitute for noble metal catalysts in the future.

The methods of preparation molybdenum carbide are contingently classified into three categories such as high-temperature methods, the preparation carbides in the form of films and coatings, the preparation carbides in the form of powders, particles and supported forms. These methods require the presence of high temperatures, hydrocarbon gases and programmable control.

In this work of molybdenum carbides were prepared using the mechanosynthesis. Mechanical activation of reaction mixtures was performed in a water-cooled high-energy planetary mill AGO-2 (Novits Ltd., Novosibirsk, Russia).

The initial compounds were ammonium heptamolybdate tetrahydrate, zirconium nitrate, nickel nitrate and carbon black. Carbon black had the aggregate size of 18-25 nm and specific surface area $S_{BET}$ = 100 $m^2/g$.

Carbon black was impregnated with appropriate aqueous solutions of initial compounds using the incipient wetness method. Mechanical activation of the starting mixture was carried out at 1000 $m/s^2$ acceleration of milling bodies for 30 min, the ball-to-powder mass ratio - 1:40.

The effect of conditions mechanical activation on the formation of molybdenum carbide was examined. The morphology, composition and structure of carbide-containing composites have been studied.

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# Conversion of natural gas and methanol on the pentasil–type zeolites modified by Zr and W nanopowders

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The study of the natural gas and methanol conversion may help to solve one of the global issuesthat are related toobtain alternative raw materials for petrochemical industry [1-3]. The aromatization process of light hydrocarbons carried out in the presence of various catalytic systems and HZSM-5 type of high-silica zeolites are considered the most effective systems among them. The usages of these catalysts differ greatly with high activity and selectivity, which makes the aromatization processes of light hydrocarbons perspective for industrial purposes [4, 5].

The aim of this paper was to study the effect of nanosized powder (NPR) additives Zr and W on acidic and catalytic properties of HZSM-5 zeolitesin the aromatization processes of natural gas and methanol.

The nanosized powders of Zr and W were obtained by dispersing metal wires with high power electrical impulses. Conversion of natural gas and methanol was carried out on a fixed vertical down-flow quartz reactor with 5 $cm^3$ catalyst layer at the atmospheric pressure. Conversion of natural gas was studied in the range of 600-750 °C temperature and the volume of feed rate was 1000 $h^{-1}$.

The conversion of natural gas and the selectivity of aromatic hydrocarbons (ArH) enhances while the process temperature rises. The conversion of natural gas in the presence of W-containing zeolite was 26.9 % yield and the yield of aromatic hydrocarbon reaches to 21.1 % at a temperature of 750 °C. It should be noted that when the HZSM-5 modified with tungsten, the selectivity of aromatic hydrocarbons is sharply increased throughout the temperature range. Thus, the selectivity of aromatic hydrocarbons in the investigated temperature ranges over HZSM-5 and 4.0 wt. % W/HZSM-5 were 36.7-46.2 % and 69.9-78.4 %, respectively. The main liquid yields of the reaction were benzene and naphthalene, and the concentration of them significantly rises by the increasing process temperature in gaseous products, the concentration of hydrogen increases and the amount of alkanes and alkenes decreases by the enhancement of reaction temperature.

Thus, the highest activity and selectivity in the formation reaction of ArH from natural gas havehad zeolite catalyst containing Zr and Wnanopowders 1.5 and 6.0 wt. % amount of respectively.

Thus, the modification of zeolite with zirconium and tungsten leads to redistribution of its acid sites by force and the formation of new active centers. Due to this point the ratio of weak acid centers to strength centers changes, which affects its catalytic properties in transformation of natural gas and methanol. A certain combination of weak and strong acid centers is necessary to obtain an effective catalyst for the conversion of natural gas and methanol to aromatic hydrocarbons, which is achieved by controlling the amount of modifiers in the catalytic system.

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# Сравнение каталитической активности $Ca(OH)_2$ и $Ba(OH)_2$ в реакции альдольной конденсации ацетона

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Основное количество ацетона производится совместно с фенолом, которые, главным образом, перерабатываются на получение бисфенола-А. При синтезе бисфенола-А фенол и ацетон вступают в реакцию в мольном соотношении 2/1, т.е. появляется излишек ацетона. В зависимости от конъюнктуры рынка, излишек ацетона реализуется через рынок и, в основном, потребляется в производстве лакокрасочных материалов. Наиболее рентабельным направлением переработки ацетона является производство более дорогого продукта, например, диацетонового спирта, получаемого реакцией альдольной конденсации ацетона.

Кинетические особенности самоконденсации ацетона таковы, что в присутствии катализатора основного характера достаточно быстро достигается равновесная концентрация диацетонового спирта, составляющая 2÷7 %. В зависимости от температуры и природы катализатора в системе устанавливается равновесие с образованием главных продуктов – диацетонового спирта и оксида мезитилена.

В данной работе проведены результаты исследования сравнительной активности $Ca(OH)_2$ и $Ba(OH)_2$ в условиях при постоянной циркуляции отгоняемого из реакционной смеси ацетона через слой катализатора в изотермическом режиме (25 °C) без выделения диацетонового спирта. Селективность образования спирта в присутствии $Ca(OH)_2$ и $Ba(OH)_2$ составляет 92 и 98 %, соответственно. По мере протекания процесса активность катализаторов (съём диацетонового спирта) несколько падает с выходом на стационарную величину для соответствующих катализаторов 0.127 и 0.285 г/г-кат.час.

Было проведено усовершенствование реакторного блока и таблетирование соответствующих катализаторов, что позволяет сохранить их активность в течение длительного периода, а также постоянно выделять диацетоновый спирт из реакционной массы с высокой степенью чистоты. Полученные результаты могут быть масштабированы на уровень пилотных установок с дальнейшим переходом на промышленный процесс.

# Alkylation of aromatic hydrocarbons with ethanol and isopropanol on modified pentasils

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In recent years, high-silicon zeolites of the pentasil type have been widely studied as catalysts for the production of para- substituted alkylaromatic hydrocarbons. Due to the presence in the pentasil structure of regular canal-shaped micropores of elliptical cross section with an average cross section of 0.55 nm, they are of great interest as promising catalysts for the production of parasubstituted hydrocarbons [1-4].

In connection with this, the purpose of this work was to study the influence of nature and the concentration of various modifiers [Zn, Cd, Sc, REE] on the physicochemical and parasectivities of H-pentasil in the alkylation of aromatic hydrocarbons with $C_6$-$C_7$ ethanol and isopropanol.

The catalysts were prepared on the basis of a HTS type zeolite with a $SiO_2$ / $Al_2O_3$ molar ratio of 33, which was converted to the H form by ion exchange and heat treatment. Catalysts modified with 1.0-10.0 % by weight modifiers were prepared by impregnation using aqueous solutions of zinc nitrates, cadmium, scandium and rare earth elements (REE).

The experiments were carried out on a stream type installation with a stationary catalyst bed at atmospheric pressure in a hydrogen stream in the temperature range 300-400 °C and a molar ratio of AS: an alcohol of 2:1.

It is established that modifying H-pentasil with modifiers leads to a decrease in the concentration and strength of strong proton centers and the formation of new stronger aprotic centers. As a result of the chemical interaction of the modifiers with the zeolite, several types of catalytic centers are formed: isolated metal ions in various ion exchange positions of the zeolite of metal oxide nanoparticles localized inside or on the outer surface of zeolite crystals, which leads to a change in its porous structure and catalytic properties. At modifier concentrations above 2.0 wt %, are observed a noticeable decrease in the pore volume of the zeolite and an increase in p-selectivity in the alkylation reactions of aromatic hydrocarbons with ethanol and propanol. The selectivity for p-ethyltoluene is 72.5-75.3 % on H-pentasils containing 10.0 % by weight of the modifier.

Based on experimental data, the main reason for the increase in the paraselectivity of H-pentasil when modifying it with modifiers is a decrease in the concentration of strong proton centers, the formation of stronger aprotic centers, and the formation of metal oxide nanoparticles localized inside and at the pore mouths, leading to a decrease in pore volume zeolite.

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# Interaction of palladium precursors with surface of aluminum oxide of catalyst of selective hydrogenation

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Palladium catalysts supported on the surface of aluminum oxides are the most widely used systems in the processes of selective hydrogenation of acetylene hydrocarbons to olefin containing streams [1-3]. These catalysts are bifunctional systems whose properties are determined by the characteristics of aluminum oxide and deposited metal particles [4, 5]. Aluminum oxide, having a certain pore structure and acid-base properties, provides diffusion of the reaction components and fixing of the active component. The highly dispersed state of the metal determines the manifestation of two effects: the metal-carrier interaction and the size effect [6, 7]. These effects and their contribution to the electronic and geometric characteristics of the active component can be varied at different stages of catalyst synthesis. At the same time, the properties of the active component are, to the greatest extent, laid already at the stage of depositing palladium salts from impregnating solutions on the surface of aluminum oxide [8, 9]. This determines the importance of studying the process of adsorption of palladium salts on the surface of an alumina carrier and the intermediate forms of metal compounds formed at the same time.

It is shown that the rate of adsorption of palladium acetate from a solution of organic solvent to the surface of aluminum oxide is higher than for palladium acetylacetonate.

Based on the data of the method of temperature-programmed reduction combined with mass spectroscopy studied form of palladium salts produced by applying to the surface of alumina. Analysis of the mass spectra shows that for palladium acetate deposited on alumina, a wide range of intermediate forms of the metal salt is characteristic. Unlike palladium acetylacetonate has a narrower forming surface fragments, which are characterized by a strong interaction with the surface centers alumina. This leads to the formation of palladium particles with a smaller diameter and lower electron density, compared to metal particles formed from palladium acetate.

Analysis of the data pulse chemisorption of carbon monoxide and the catalytic test in the selective hydrogenation of methylacetylene and propadiene palladium particles formed in the temperature range corresponding to the decomposition of the metal salts, held isothermal treating the alumina carrier with the active component applied salts at temperatures of 150, 300, 400, 500 and 600 °C showed that a stronger interaction of palladium acetylacetonate with surface centers of aluminum oxide leads to the formation of particles metal with a smaller diameter, compared with systems of palladium acetate. This leads to a lower electron density of the metal particles of palladium acetylacetonate having lower activity, compared with the metal particles formed from palladium acetate.

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# The study of catalysts $Pd/SO_4/ZrO_2/Al_2O_3$ with additives of hydrofluoric acid for n-hexane isomerization

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The introduction of the new technical regulations tightens the requirements for automotive fuel for the content of aromatic hydrocarbons [1]. Reduction of the content of aromatic hydrocarbons in gasoline is aimed to decrease the toxicity of exhaust gases of vehicles. Isomerization of pentane-hexane fraction is one of perspective processes of production of commercial gasoline with low content of aromatic hydrocarbons. This process allows to obtain high-octane gasoline components from low-octane straight fraction $C_5$-$C_6$.

Currently, effective catalytic systems based on zirconia are promising for the isomerization of $C_5$-$C_6$ alkanes. These catalysts show high activity and selectivity, have the resistant to impurities in the feedstock and operate in thermodynamic favorable range of temperatures 140-200 ºC to achieve high yields of the target products [2].

Catalytic compositions based on $SO_4/ZrO_2$ modified by metal cations have been the subject of research by many authors, information of this works is given in the reviews [3, 4]. On the contrary, anionic modification of these systems is poorly studied.

In this work catalysts $Pd/SO_4/ZrO_2/Al_2O_3$ with additives of hydrofluoric acid in an amount of from 1.7 wt. % to 5 wt. % were synthesized. The catalyst $Pd/SO_4/ZrO_2/Al_2O_3$ without acid addition was used as a reference sample. The concentration of palladium in the catalysts was 0.5 wt. %.

Catalytic tests were carried out in a flow fixed-bed reactor under the following conditions: reaction temperature 140–200 °C, hydrogen pressure 1,5 MPa, liquid hourly space velocity (LHSV) 2 $h^{-1}$ and $H_2/n$-hexane molar ratio 3/1.

It was shown that the addition of hydrofluoric acid in an amount of 2.8 and 5 wt.% leads to a decrease in the specific surface area of the samples from 75 $m^2$ (without addition HF) to 52 and 55 $m^2$, respectively. It was found that catalytic performance of samples with additives of hydrofluoric acid are higher than for unmodified sample. The best performance at the isomerization reaction of *n*-hexane is achieved on the catalyst with the HF addition equal to 2.8 wt. %. At the reaction temperature 140 °C the conversion of *n*-hexane is 87.6 wt. %, yield of isohexanes – 86.1 wt. %, the content of the dimethyl-substituted isomers in the sum of hexane isomers –36.3 wt. %.

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# Alumina-supported sulphated zirconia catalysts modification by tin

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Process of an isomerization of fractions $C_5$-$C_6$ is the important process of the modern oil processing allowing to receive high-octane components of the gasolines corresponding to a class 5. Catalysts on the basis of sulfated zirconia with platinum as the most promising.

In work the put sulfated zirconia catalysts on alumina modified by additives of tin which was entered at different stages of preparation of catalysts are investigated: in aluminum hydroxide, on the $\gamma$-$Al_2O_3$ support, on the $\gamma$-$Al_2O_3$ porous matrix on which zirconium sulfate was deposited after its calcination at 750 °C. At different ways of introduction of tin there was a research influence of the precursor of tin (used tin salts: tin chloride (II) and (IV), tin sulfate (IV), hydroxide of tin (IV)) and amount of the entered tin (0,25; 0,5; 1 wt. %).

The resulting catalysts were investigated by a low-temperature nitrogen adsorption, XRD, and tested in the isomerization reaction of n-hexane. Isomerization of n-hexane was carried in flow reactor at $H_2$ pressure 1.5 MPa in temperature range 140-220 °C.

Results of X-ray diffraction analysis show that in the supported catalyst only the active tetragonal phase t-$ZrO_2$ is observed. In sample with the different content of tin introduced into aluminum hydroxide from tin hydroxide, peaks corresponding to a tetragonal phase of dioxide of tin appears. The intensity of the peaks increases with an increasing the content of tin.

According to catalytic tests of the supported catalysts with the different content of tin it is visible that the content of tin promoting the highest yield of the sum of isomers of hexane is 0,25-0,5 % wt. at introduction of tin to aluminum hydroxide from tin hydroxide. On the catalyst with the active $SO_4/ZrO_2$ component the best characteristics are obtained at introduction of 0,5-0,75 % wt. tin from $SnCl_4$ solution. On the catalyst the $\gamma$-$Al_2O_3$ support impregnated by solution of tin salts, the best results are achieved when using as the precursor of $Sn(SO_4)_2$. Yield of the sum of isomers reach 75% wt. On the received catalytic properties, the supported catalysts approach the modern production catalysts of an isomerization.

*Physicochemical testing of the catalysts was carried out at the facilities of the Omsk Regional Shared Equipment Center SB RAS.*

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# SECTION 3

## RESEARCH METHODS IN CATALYSIS

# Peroxide oxidation of methane to formic acid and other oxygenates over Fe-containing zeolites

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Methane is an abundant natural resource. Moreover, $CH_4$ is permanently recovered via the global natural's cycle of carbon (ca. $10^9$ ton per year) [1] what makes methane a renewable compound [1]. All the advantages of $CH_4$ make it very attractive for overcoming energetic, resource and ecological problems. However, methane is a very inert molecule, as the dissociation energy of a C–H bond equals to 440 kJ $mol^{-1}$ [2]. Thus, the chemical activation of methane is a great fundamental challenge which has to be solved for sustainable future [3]. Fe-containing zeolites were previously shown to be perspective catalysts of the peroxide oxidation of methane to methanol and/or formic acid under mild conditions [4]. In this connection, the present study was aimed at revealing the influence of Fe-ZSM-5 zeolite morphology (the crystallite size and texture properties) and structure of Fe-containing species inside the zeolite framework on catalyst selectivity to partial peroxide oxidation of methane to methanol and formic acid. The catalysts were characterized by XRD, ICP-OES, SEM, UV-vis DR, ESR, $NH_3$-TPD, $^{27}$Al MAS NMR, $N_2$ adsorption.

All the catalysts were tested in the hydrogen peroxide oxidation of methane at 50 °C. The catalysts of different morphology (nanocrystals, microcrystals, and bulk commercial sample) were studied in the reaction before and after activation of the Fe-containing active sites with an oxalic acid solution. The activation ensures the transformating the oxygen coordination sphere of iron cation from tetrahedral framework to octahedral extraframework. The results obtained demonstrated the dependence of the catalyst activities and selectivities to the main reaction products (methanol, formic acid, and carbon dioxide) on three key factors: the external surface area/crystallite size, concentration of Brönsted acid sites, and concentration/size of Fe oxide clusters. Activation of all the catalysts with oxalic acid caused a decrease in the selectivity of the methane oxidation to $CO_2$ and methanol. At the same time, the selectivity of formic acid formation increased, probably due to an increase in the quantity of oligomeric Fe oxide clusters (UV-vis DR and ESR data) during the activation. There also was observed an increase in the acid sites of the catalysts (TPD-$NH_3$ data) which can produce stable formate complexes. Inspection of correlations between the catalyst selectivity and the key factors discussed above as well as studying oxidation of methanol and formic acid substrates over the non-treated and activated catalyst allowed one to suppose different pathways to the formation of methanol/$CO_2$ and formic acid from methane over Fe-ZSM-5 catalysts. This hypothesis showed the methane and formic acid oxidation via heterogeneous route on the binuclear and/or oligomeric oxo-clusters of Fe-ions. The oxidation of methanol is more probably to follow the free radical mechanism. It should be emphasized that ca. 75% of $H_2O_2$ was consumed for methane oxidation over the activated commercial catalyst and only the rest for the concurrent decomposition of hydrogen peroxide itself.

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# Effect of graphitization and oxidative treatment on the thermal stability of the Pt/Sibunit catalyst in a reducing atmosphere

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Catalysts based on platinum metals supported on carbon are widely used in industrial processes, including reactions such as selective hydrogenation (C = C, C ≡ C bonds), hydrogenation of aromatic hydrocarbons, dehydrogenation (C-H bonds), oxidation of CO, dehydrochlorination, and as catalysts for low-temperature fuel cells.

At relatively low temperatures in the reducing environment, the Pt / C catalyst systems show rather high stability. However, at increased temperatures and hydrogen-containing atmosphere at places of the metal-support contacts reacts hydrogen, activated by metal, interacts with the carbon, resulting in the formation of methane (methanation of the carbon support). As a result, this undesirable process adversely influences on the entire catalytic system, leading to sintering of the active component, gradual destruction of the support and deactivation of the catalyst. In this regard, an increase in the thermal stability of catalytic Pt / C systems in a reducing medium is an urgent task.

The purpose of this work was to study the influence of pretreatments of the carbon support "Sibunit" (1 - graphitization - calcination at 1900°C in nitrogen, 30 minute.; 2 - oxidation treatment - keeping of support in concentrated nitric acid for 1.5 hours) on the thermal stability of catalytic system Pt/C in an atmosphere containing hydrogen.

The thermal stability of the Pt/C systems in the reducing atmosphere was studied by two modes: 1. The thermo programmed - quartz reactor with the sample, kept in a helium flow at 120°C for 10 minutes and then cooled to 50°C, after that hydrogen was supplied and the temperature was increased to 500°C (10°C/min); 2. Isothermal - the reactor with the sample was heated to 500°C (10°C/min) in a flow of helium. At 500°C, hydrogen was supplied and the sample was kept under these conditions for up to 3 hours. At the outlet of the reactor, the mixture was analyzed by means of a gas chromatograph with a flame ionization detector.

It has been determined that the oxidative treatment does not have any significant effect on the thermal stability of the Pt/C catalyst. In contrast, graphitization of Sibunit increases the thermal stability of the Pt/C system, but dramatically decreases the specific surface of the support, which subsequently proves to be a favorable condition for the formation of large metallic Pt particles.

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# Comparison of supported $CrO_x$ catalysts in non-oxidative and oxidative dehydrogenation of light alkanes

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A growing demand in the obtaining of high purity olefins requires new technologies of their production in addition to traditional steam and catalytic cracking methods. Olefins are widely used in chemical and pharmaceutical industry to produce a wide range of valuable chemicals. For these purposes, catalytic non-oxidative (DH) and oxidative (ODH) direct dehydrogenation of alkanes into olefins represent wide scientific interest. DH of alkanes is a promising method due to high selectivity toward olefins. In turn, ODH with $CO_2$ as a mild oxidant is also prospective due to possibility of shifting of the dehydrogenation reaction equilibrium and $CO_2$ utilization. Both DH and ODH pathways strongly depend on red-ox properties of support and active component. To date, different types of mixed oxides [1, 2] have been studied as catalysts for these processes. In spite of toxicity of chromium compounds, Cr-containing catalysts remain one of the most active among the catalysts for DH. The use of $CrO_x$ as an active component supported on alumina is caused by ability to multiple and reversible oxidation-reduction ($Cr^{V/VI}\leftrightarrow Cr^{II/III}$). Supported Cr-containing catalysts also show high activity in ODH-$CO_2$ of propane and isobutane. However, the use of oxide supports for Cr catalysts with active oxygen and red-ox properties is preferable for higher activity and stable operation of the catalyst. Alumina shows poor red-ox ability, while $ZrO_2$, $CeO_2$ and mixed ceria–zirconia oxides are the best candidates as supports for ODH catalysts due to their unique red-ox properties. Thereby, the purpose of the present work is to compare the activity of Cr-containing systems on different supports in non-oxidative and oxidative dehydrogenation of alkanes.

$\gamma$-$Al_2O_3$, $CeO_2$, $ZrO_2$, $Ce_xZr_{(1-x)}O_2$, and $\gamma$-$Al_2O_3$, modified with $ZrO_2$ and/or $CeO_2$, were used as supports. Cr-containing catalysts with Cr loading corresponding to a monolayer (5 $at_{Cr}/nm^2$) were prepared by incipient wetness impregnation of supports using aqueous solution of $H_2CrO_4$. The catalysts were dried at 80 °C for 12 h and calcined at 600 °C for 4 h. The catalysts were characterized by low-temperature $N_2$ sorption, XRD, TPR, DRS, RS and tested in DH of isobutane and ODH-$CO_2$ of ethane.

According to the results obtained, the state of Cr on the surface is different over different supports. The formation of $\alpha$-$Cr_2O_3$ particles is observed only for the $CrO_x/CeO_2$ catalyst. TPR-$H_2$ results show that the $CrO_x/ZrO_2$ and $CrO_x/Ce_xZr_{(1-x)}O_2$ contain the highest amount of red-ox $Cr^{5+/6+}$ species. These catalysts are the most active in i-$C_4H_{10}$ dehydrogenation. Thus, mainly chromium state affects on the catalyst activity in DH of isobutane. The modification of $\gamma$-$Al_2O_3$ by $ZrO_2$ and/or $CeO_2$ leads to an increase of $Cr^{5+/6+}$ parts and growth of activity in DH of i-$C_4H_{10}$ in comparison with unmodified $CrO_x/Al_2O_3$ catalyst. However, in the case of ODH-$CO_2$ of ethane the reaction pathway, activity and stability of the catalyst depend on both chromium state and support features (acid-base and red-ox properties) [3]. The $CrO_x/\gamma$-$Al_2O_3$ and $CrO_x/ZrO_2$ catalysts exhibited the highest ethylene formation rates, but the reaction followed different pathways. On $CrO_x/\gamma$-$Al_2O_3$ catalyst, ethylene is formed via direct dehydrogenation of ethane accompanied by RWGS, while on $CrO_x/ZrO_2$ ethylene is formed via selective ODH. Addition of $ZrO_2$ and/or $CeO_2$ to $CrO_x/Al_2O_3$ catalyst results in selective ODH. For $CrO_x/ZrO_2/Al_2O_3$ catalyst, ethylene is additionally formed via selective ODH reaction, while non-selective and/or dry reforming reactions take place on $CrO_x/CeO_2/Al_2O_3$ as shown by the higher CO formation rate.

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# Anthracene coking over catalysts based on carbon nanotubes

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Nowadays, due to depletion of light hydrocarbon reserves, the share of heavy crude oil at refineries and, accordingly, the volume of obtained oil residues increase. Therefore, the task of improving existing technologies aimed at increasing the processing depth of heavy oils and oil residues, and developing new ones is very relevant [1]. Therefore, more attention is attracted to coking, which converts heavy feedstocks into hard coke and lower-boiling hydrocarbon products. Delayed coking is the most common coking method. Delayed coking units mostly produce sponge coke. Needle coke, which is produced from raw materials with high aromatic content, is a more valuable type of petroleum coke. Its name originates from its structure consisting of crystals with elongated shape.

The present study was devoted to the development of methods for regulating the morphological and crystalline structure of coke. An aromatic compound with condensed nuclei anthracene was used as a model raw material. Coking was carried out in an autoclave at 400-650 °C for 2 hours. Both neat anthracene and anthracene mixed with a catalyst were subjected to coking. Carbon nanotubes (CNTs) and CNTs with deposited cobalt oxide (0.5 wt.% CoO-CNT) were used as catalysts.

The conducted studies showed that the addition of CNT or CoO-CNT accelerates the coke formation. For instance, in the case of pure anthracene the process begins at temperatures above 500 °C. In systems containing a catalyst: 10 mass% of CNT-anthracene or 10 mass% of CoO-CNT-anthracene coking starts at 450 °C. Redistribution of hydrogen present in anthracene occurs during coking. Light $C_1$-$C_3$ hydrocarbons are released along with the coke. The morphology of the forming coke changes significantly. In the case of neat anthracene, spherical particles of poorly crystallized carbon about a micron in size are formed. Addition of carbon nanotubes leads to the formation of a carbon coating that covers the CNT surface. Consequently, CNTs act as nuclei for the formation of the coke phase.

Cobalt oxide is reduced during coking to cobalt metal and catalyzes the growth of carbon nanofibers following the carbide cycle mechanism [2].

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# The influence of the solvent nature on glyoxal disproportionation in glycolic acid using Sn-MFI zeolite as a catalyst

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Recently, the metal-containing high-silica zeolites have gained a significant interest as heterogeneous catalysts for liquid-phase processes [1-4]. Such materials are used as catalysts for keto-alco transformation, including isomerization of ketoalcohols [5], disproportionation of α-dicarbonyls [2], MPV-type reactions [3], alkene epoxidation [4], cycloketone-lactone oxidation [6]. The main advantages of these catalysts are a homogeneity of their active centers and a microporous structure that cause high selectivity in the abovementioned processes. According to the literature, the tetrahedrally coordinated tin cation in the zeolite lattice acts as an active center [7]. The intramolecular glyoxal (GLY) disproportionation into glycolic acid is the most selective and irreversible reaction which may be carried out over Sn-containing MFI-type catalysts. Ohshima et. al. [8] proved that the reaction mechanism passes through a hydride shift. There is an information about the opportunity of GLY disproportionation reaction to occur using different proton solvents such as alcohols (methanol, ethanol, and butan-1-ol) [2]. The present work is focused on the influence of water–acetonitrile binary mixture on the GLY disproportionation kinetics with the Sn-MFI-140 used as the most active and selective catalyst amongst the obtained mesoporous silica-based tin-incorporated zeolite materials.

Batch catalytic tests were carried out under argon cushion in the 40 cm$^3$ thick-walled glass vials dipped in a heating stirrer at 343 K. The vials were loaded with 0.3 ml of 1M glyoxal solution prepared from 40 %wt. glyoxal (Sigma-Aldrich), 10 mg of the Sn-MFI catalyst (Si/Sn = 140), and 29.7 ml binary solvent with a different molar ratio. The glyoxal/tin ratio was 259 in the final reaction mixture. In reaction products glycolic acid (GA) was isolated by high-performance liquid chromatography (HPLC) in a Shimadzu LC-20C system equipped with a Phenomenexe Rezex ROA-H+ column heated at 313 K and a UV detector at 210 nm using an aqueous eluent of 0.005 M $H_2SO_4$ (pH 2.30) flowing at 0.9 cm$^3$ min$^{-1}$. Glyoxal was determined by addition of Girard-T reagent in a 0.5 M $H_3PO_4$ water solution. After derivatization, GLY-Girard-T adduct was isolated by the high-performance liquid chromatography (HPLC) in a Shimadzu LC-20C system equipped with a Zorbax SB-Aqua column heated at 303 K and a UV detector at 295 nm using an aqueous eluent of 0.005 M $H_2SO_4$ (pH 2.30) flowing at 1.0 cm$^3$ min$^{-1}$.

It was shown that the reaction of GLY disproportionation to glycolic acid on the Sn-MFI-140 catalyst occurs quantitatively. The rate of GLY transformation in water–acetonitrile binary mixture rises with the increase in the concentration of acetonitrile in the mixture and depends on the dielectric constant of the system. The maximal rate is observed for the water–acetonitrile molar ratio of 1/8. The effective rate constant logarithm for glyoxal disproportionation to glycolic acid is straightened in the Kirkwood equation coordinates, which evidences on the presence of non-specific interactions between the solvent and the activated complex.To study the influence of the adsorption of glyoxal and glycolic acid the experiments on GLY and GA adsorption on the surface of the studied catalyst have been carried out. Unlike glycolic acid, glyoxal adsorption was observed in both solvents. The adsorption degree of GLY in acetonitrile was 32 times higher than in water. The tentative scheme of glyoxal transformation into glycolic acid over the tin-containing active site will be discussed.

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# The Reduction Temperature Influence on the Active Component State and Catalytic Properties of Pd-M/Sibunit (M: Ag, Zn, Ga) in Liquid-phase Selective Hydrogenation of Acetylene

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Liquid-phase selective hydrogenation of acetylene is the key stage of GTL (‘gas-to-liquid’) technology for the natural or associated gas components converting to ethylene and/or to the high-octane components of motor fuel [1, 2]. Acetylene obtained by oxidative pyrolysis of natural (associated) gas is absorbed by selective solvent and converted to ethylene by hydrogenation on supported palladium catalysts. To increase of the process selectivity and the resistance of the samples to deactivation, palladium is modified by the second metal (elements of IB, IIB or IIIA subgroups). However, the literature data on the active component composition and structure influence for such systems on the catalytic properties in this process are limited to several patents [1, 2]. The aim of this work is to investigate the palladium and the modifier precursors reduction temperature ($T_{red}$) effect on the active component state and the catalytic properties of 0.5 % Pd-M/C (M: Ag, Zn, Ga) (Pd:M = 1:1) in the liquid-phase hydrogenation of acetylene to ethylene.

Carbon composite Sibunit ($S_{BET}$ = 325 $m^2/g$) was used as a support. Samples of the catalysts were prepared by an incipient wetness impregnation with joint aqueous solution of palladium and modifier nitrates with following stages of drying and reduction in a hydrogen stream (3 h). $T_{red}$ was varied from 200 to 500 °C. Hydrogenation of the model gas mixture (4 % vol. $C_2H_2$ and 96 % vol. $H_2$) was carried out at 55 °C in N-methylpyrrolidone medium in the shaker-type flow reactor.

The increasing of the $T_{red}$ for Pd-M/C catalysts from 300 to 500 °C leads to the decreasing in the catalytic activity but the selectivity is increasing (by 20-25 %). According to results of the ethane hydrogenolysis on Pd/C samples, the decreasing in the catalytic activity is related to the drop in the surface palladium concentration due to the sintering of initial nanodispersed particles. Using the XRD SR and XAFS data, it was found that the increasing in hydrogenation selectivity for the samples prepared at 500 °C is due to the formation of bimetallic PdZn, $Pd_xGa_y$ and PdAg nanoalloys. It is lead to significant increase of the distance between neighboring atoms of palladium from 2.72 Å for Pd/C sample to 2.82 – 2.89 Å for the modified Pd-M/C catalysts, which is accompanied with a change in geometry of acetylene adsorption (predominantly in π-bonded state) and, possibly, lead to increasing of the target product yield [3]. The interaction of Pd and Ag occurs even at $T_{red}$ = 300 °C and bimetallic $Pd_{0.12}Ag_{0.88}$ and $Pd_{0.52}$ $Ag_{0.48}$ particles are formed. With the growth of the $T_{red}$ to 500 °C their composition is come near to the $Pd_{0.57}Ag_{0.43}$, which is accompanied by increasing in reaction selectivity from 43 to 58 %. Transformation of the active component structure in Pd-Zn- and Pd-Ga-catalysts with the formation of bimetallic PdZn and $Pd_2Ga$ nanophases occurs at T = 500 °C. Based on the analysis of the XAFS spectra, it is assumed that the PdZn particles have a «core-shell» structure where the palladium cores are coated by the layer of joint PdZn phase. Investigation of the Pd-Ga catalysts is complicated by the addiction of Ga to oxidize during the operating with the samples in air.

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# The causes of the modifying effect of phosphorus on the properties of palladium catalysts in the hydrogenation of acetylenic compounds

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Chemoselective hemihydrogenation of multiple bonds in acetylenic compounds (unsaturated hydrocarbons and alcohols) is an important fundamental problem, the solution of which is also of great practical importance [1]. Conventional approaches used to increase the chemoselectivity of metal catalysts lead to a decrease in catalytic activity [2, 3]. We studied the Pd-P nanoparticles as active and selective catalysts for the hydrogenation of alkynes and acetylenic alcohols. The introduction of phosphorus at the stage of reduction of the palladium precursor by hydrogen increases the catalytic activity in the hydrogenation of disubstituted and terminal alkynes and acetylenic alcohols by 4-8 times (TOF = 870 $\text{min}^{-1}$, T = 30 °C, $P(H_2)$ = 2 atm) in comparison with Pd-black, while retaining a 93-96 % selectivity to alkenes and allylic alcohols. By varying the P/Pd ratio, it is possible to purposefully change the ratio between the hydrogenation rates of the starting monosubstituted alkyne and the resulting alkene. The nature of the Pd-P catalysts as well as the causes of the modifying effect of phosphorus on catalysts have been established by several analytical techniques such as HRTEM, HAADF STEM, XRD, EDS, XPS. It is shown that the growth of the activity of Pd-P catalysts in the hydrogenation of acetylenic compounds is due to the action of both geometric and electronic factors. Palladium clusters formed along with palladium phosphides in the low-temperature synthesis of Pd-P catalysts are carriers of catalytic activity under mild conditions in the hydrogenation of unsaturated compounds. An experimental substantiation of the influence of the palladium clusters size on the hydrogenation rates ratio of starting alkyne and formed alkene is obtained. It is the formation of small palladium clusters (0.6-1 nm) in Pd-P containing nanoparticles (P/Pd = 1) that is responsible for the change in the ratio of the hydrogenation rates of the triple and double bonds with increasing P/Pd ratio. General schemes of formation and functioning of Pd-P containing nanoparticles are considered. It is shown that the increase in the size of small palladium clusters during the functioning of Pd-P catalysts (P/Pd = 1-1.5) and their diffusion onto the surface of nanoparticles is the reason for the observed autoacceleration.

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# Influence of Rh-$CeO_2$ interaction on RedOx properties of the catalysts

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Catalysts based on rhodium and ceria are widely used in many important catalytic reactions including conversion of exhausts gases, preferential CO oxidation, ethanol steam reforming, *etc*. The catalytic activity of this system is largely determined by the nature of the metal-support interaction. In the present work, we studied Rh/$CeO_2$ systems with a variation of a degree of a metal-support interaction in order to establish its influence on the RedOx properties of the catalysts.

Rh-doped $CeO_2$ powder catalysts were prepared by co-precipitation from nitrates and calcined over a wide temperature range 450-1000 °C. For the synthesis of the model system, the technique of radio-frequency discharge sputtering (RF-sputtering) of the Rh electrode in an oxygen atmosphere on a surface of $CeO_2$ was applied. The physicochemical properties were analyzed by a complex of methods (X-ray powder diffraction, Transmission electron microscopy, X-ray photoelectron spectroscopy, Raman spectroscopy) in correlation with their RedOx properties (reactivity towards CO oxidation and re-oxidation by molecular $O_2$).

An investigation by physicochemical methods revealed the homogeneous distribution of rhodium $Rh^{3+}$ ions and/or $RhO_x$ clusters in the $CeO_2$ lattice in catalysts prepared by co-precipitation method. When the Rh electrode was RF-sputtered in $O_2$ on the $CeO_2$ surface, a composite $RhO_x/CeO_2$ system was formed, consisting of $RhO_x$ nanoparticles in contact with the surface of $CeO_2$ particles providing formation of Rh-$CeO_2$ interface but without substitution of $Ce^{4+}$ ions by $Rh^{3+}$ in $CeO_2$ lattice.

Rh-doped $CeO_2$ catalysts and $RhO_x/CeO_2$ model systems demonstrated different RedOx properties. Interaction of $RhO_x/CeO_2$ system with CO resulted in $Rh^{3+}$ reduction at temperature higher 200 °C with a complete reduction to $Rh^0$ species at 450 °C. The reduction of $Ce^{4+}$ species upon CO exposure was observed as well, but with less efficiency. The $Ce^{3+}$ fraction reached ~18% after interaction with CO at 250 °C and remained unchanged with further temperature increase. For Rh-doped $CeO_2$ catalysts, interaction with CO resulted in a reduction of both $Ce^{4+}$ and $Rh^{3+}$ species already at low temperatures ($T<150^0C$) with substantial reduction of $Ce^{4+}$ species even at room temperature. The $Ce^{3+}$ fraction reached ~18% at T=50 °C and ~35 % at T=450 °C. Complete reduction of $Rh^{3+}$ species was observed at 350 °C.

Thus, it can be concluded that stabilization of $RhO_x$ nanoparticles on the surface of $CeO_2$ leads to Rh-$CeO_2$ interfacial interaction, which results in activation of the oxygen of ceria at Rh-$CeO_2$ interface. However, it cannot provide the activation of $CeO_2$ lattice oxygen at low temperatures. In order to activate oxygen in Rh/$CeO_2$ system in the temperature range below 100 °C, the presence of dispersed rhodium $Rh^{3+}$ species which substitute $Ce^{4+}$ ions in $CeO_2$ lattice is required.

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# The one-pot conversion of renewable polysaccharides to polyols in the presence of Ru/CsHPAs catalysis

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The gradual depletion of high-quality and available fossil sources of oil, gas and negative impact of traditional chemical industries on the environment causes ones to develop alternative technologies based on transformations of new types of sources. Renewable biomass is the most perspective alternative raw material for the production of valuable chemicals, for example, important polyalcohols like sorbitol and xylitol which are widely- used at pharmaceutics and food industry as sweeteners, and drug components. The one-pot hydrolysis-hydrogenation of the most widespread natural polysaccharides (cellulose, starch, xylan) seems to be a promising and effective alternative method to form sorbitol and xylitol.

Polyalcohols are the products of two sequential chemical steps: hydrolysis of biomass and hydrogenation of biomass derivatives. Acid catalyst must be used for hydrolysis of polymers (cellulose, starch or xylan) to get respective monosaccharide (glucose or xylose). In that way bifunctional catalyst is needed to produce target products with high selectivity and efficacy. Cesium salts of HPA (CsHPAs) have acidic catalytic centers what makes them perspective acid solid supports. Reduction of monosaccharides proceeds over noble metal nanoparticls and ruthenium is the most perspective for that reaction. Thus, the aims of the study was the development of bifunctional catalysts Ru/CsHPAs, testing the catalysts developed in the one-pot conversion of polysaccharides (cellulose, starch or xylan) to valuable polyols of sorbitol and xylitol and revealing the influence of the catalysts' composition and morphology on the catalytic activity.

CsHPAs with the composition of $Cs_{2.1}H_{0.9}PW_{12}O_{40}$ (Cs-PW) and $Cs_3HSiW_{12}O_{40}$ (Cs-SiW) were synthesized by mixing solutions of $Cs_2CO_3$ and respective HPAs. Ru/CsHPAs were prepared via impregnation the supports by Ru precursor $Ru(NO)(NO_3)_3$. Loading of Ru on cesium salts were 1 and 3 %. A 3%Ru/C catalyst was also produced as a reference system. The catalysts were investigated by IR spectroscopy, $N_2$ absorption, XRD, AES-ICP, TEM and were tested in the one-pot hydrolysis-hydrogenation of mechanically activated crystalline cellulose, starch and xylan under hydrothermal conditions (150-190 °C, $H_2$ pressure 5MPa). The concentrations of products were measured by HPLC.

According to ICP-AES, the solubility of Ru, W, Cs, Si, P is low, that indicated the stability of the catalytic systems. IR spectroscopy and XRD of Ru/CsHPAs catalysts showed excellent stability of HPA structures. Addition Ru on the CsHPAs decreased the content of Brönsted acid sites, but increased the amount of Lewis acid centers on the surface of CsHPas. TEM analysis of catalysts revealed ruthenium nanoparticles size in the range of 0.9 to 1.4 nm.

Testing CsHPAs without Ru showed no support activity in hydrolysis-hydrogenation of polysaccharides. Mechanical mixture of the acidic supports with 3%Ru/C allows ones to produce the sorbitol with the low yield 8 % and high selectivity (>90%). At the same time utilization of the bifunctional Ru/CsHPAs catalysts gives high sorbitol yields (36-63 %) under high selectivity (up to 94%) from cellulose and starch. The high yield of sorbitol may be accounted for synergetic effect caused by the spatial proximity of the acidic and reducing sites on the Ru/Cs-HPAs surfaces. 1%Ru/CsHPAs is more active than 3%Ru/CsHPAs. The 1%Ru/$Cs_3HSiW_{12}O_{40}$ is the most perspective catalyst to make sorbitol from cellulose and starch. On the other hand, the hydrolysis-hydrogenation of xylan to xylitol carried out in the presence of 1% Ru/$Cs_3HSiW_{12}O_{40}$ made only 31% of xylitol yield possible under harsher conditions (10 h, 190 ° C) compared to cellulose and starch transformations (7 h, 150-180 °C). Xylan appeared to be more robust than cellulose and starch in hydrolysis-hydrogenation and more severe conditions and longer time are necessary to convert xylan.

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# Peculiarities of formation of the active surface of Cu-modified $CrO_x/Al_2O_3$ catalysts for dehydrogenation of isobutane to isobutylene

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Currently, the dehydrogenation of light paraffins is of importance for industry. This is connected with a growth in demand for olefins as the initial block for polymers and organic chemicals. In Russia, the microspherical chromia-alumina catalysts are widely used for dehydrogenation of paraffins in a fluidized bed catalytic process. However, these catalysts are characterized by high abrasive ability of microspheres, the formation of toxic catalytic dust, which pollutes the environment. The trend to complete refuse from microspherical catalysts is observed in foreign countries. As an alternative, $CrO_x/Al_2O_3$ catalysts in the fixed bed (processes Catofin and Catadiene) are used [1]. $\gamma$-$Al_2O_3$ is used as a support for these catalysts due to efficient porous structure and high thermal stability. The dehydrogenation process is carried out at high temperatures of 550-650 °C.

To increase the activity and selectivity of the catalysts different modifiers are used. The modifiers used represent alkaline and alkali-earth metals as well as metals of VIII (Fe, Co, NI) and Ib (Cu, Ag) groups are widely used to decrease the acidity of the catalysts and increase the mechanical stability of the catalyst granules. The $Cu/Al_2O_3$ materials are also used in the dehydrogenation of hydrocarbons as a heat-generating material [2]. However, an influence of copper on the $CrO_x/Al_2O_3$ catalysts for dehydrogenation of isobutane to isobutene had been poorly studied. Therefore, the investigation of the Cu addition on the state of the active component and catalytic properties in the dehydrogenation reaction is of importance. The present work is focused on the study of the effect of copper addition on the textural and redox properties of the modified alumina support and chromia-alumina catalysts on the basis thereof.

The pseudoboehmite was used as a precursor of the support ($\gamma$-$Al_2O_3$). The series of modified alumina supports (loading of Cu from 0 to 5 %wt.) were prepared by incipient wetness impregnation of boehmite by an aqueous solution of copper nitrate. Then the supports were dried at 120 °C for 12 hours and calcined at 750 °C for 6 hours. After calcination the modified supports were impregnated by an aqueous solution of chromium oxide (VI). The nominal loading of $Cr_2O_3$ in the catalysts was 4.5 %wt. Drying and calcination were carried out under the same conditions as for the supports. The structure of the prepared supports and catalysts as well as the states of Cu and $CrO_x$ were studied by low-temperature nitrogen adsorption, TPR-$H_2$, XRD, UV-vis and Raman spectroscopy. The catalytic experiments were carried out in the quartz tubular reactor with a fixed catalyst bed at 540 °C. The experiment was carried out during 3 hours with a regeneration in air and reduction in $H_2/N_2$ [3].

The introduction of copper as a modifier was shown to change the textural characteristics of the supports and catalysts. An increasing of Cu loading to up to 2 %wt. results in increasing of the $S_{BET}$ from 115 to up to 124 $m^2/g$ along with decreasing of the mean pore size. Further increasing of Cu loading to up to 2.5 and 5 %wt. leads to decreasing of the $S_{BET}$ to up to 102 and 95 $m^2/g$, respectively. The copper oxides were not detected by XRD, and only small amounts of $CuAl_2O_4$ phase was observed in the support and catalyst that indicates the formation of a layer of aluminates on the surface of the alumina support. The absence of the reflexes of chromium-containing phases in the XRD indicates the homogeneous distribution of $CrO_x$ on the support surfaces. The TPR studies show that Cu promotes a reduction of chromia at low temperatures. The growth of the catalytic activity in the isobutane dehydrogenation to isobutylene is observed for Cu-modified catalysts. The optimal Cu content for this catalyst was 2 %wt.

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# An influence of SiOH/Ag ratio on the catalytic activity of Ag/SBA-15 in low-temperature CO oxidation

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Carbon monoxide is a product of incomplete combustion of hydrocarbons, also serving as an intermediate used in reactions with hydrogen in the important industrial processes yielding the organic alcohols and unbranched hydrocarbons [1]. CO is harmful because it is a colorless and odorless gas that may cause a severe poisoning and death.The catalytic oxidation of CO over Ag/$SiO_2$ catalysts has a great practical and scientific interest. There are many factors that influence the activity of Ag/$SiO_2$ in CO oxidation, namely, the size of the Ag nanoparticles, pretreatment conditions and Ag–$SiO_2$ interactions [2]. Previously in Ref. [3] it was shown that in the case of Ag/$SiO_2$catalysts, a high activity in CO oxidation may be achieved at an optimal value of the SiOH/Ag ratio (~1.3). The aim of this work is to study the effect of SiOH/Ag ratio on the catalytic activity of Ag/SBA-15 catalysts in low-temperature CO oxidation.

The SBA-15 was synthesized by the template method according to the procedure described in Ref. [4]. The triblock copolymer Pluronic P123 (PEO-PPO-PEO) was used as a template. The prepared SBA-15 was calcined at 500, 700 and 900 $^oC$. Thus, three types of supports with different degree of calcination (SBA-500, SBA-700 and SBA-900) were obtained. The supports were characterized by low-temperature $N_2$ adsorption and temperature-programmed desorption of water. The Ag-containing catalysts were synthesized by incipient wetness impregnation method using $AgNO_3$ as a precursor (5, 10 and 15 %wt. of Ag). The catalysts were characterized by XRD, TPR, TPD methods and tested in low-temperature CO oxidation.

Using the method of low-temperature $N_2$ adsorption it was shown that with the growth ofcalcination temperature, the specific surface area ($S_{BET}$) decreased from 717 $m^2$/g for SBA-500 to 622 and 501 $m^2$/g for SBA-700 and SBA-900, respectively, without significant changing of the pore size distribution. Using TPD-$H_2O$ it was shown that the concentration of OH group on the surface of SBA-500, SBA-700 and SBA-900 was 1.45, 1.34 and 1.17 OH/$nm^2$, respectively. The catalytic activity tests demonstrated that the highest activity was achieved over the catalysts containing 5 %wt. Ag. The lowest catalytic activity was observed for the 15Ag/SBA-500 catalysts ($T_{50\%}$=124$^o$C). The 5Ag/SBA-700was the most active catalyst ($T_{50\%}$=52$^o$C) that may be related to the optimal value of the SiOH/Ag ratio for this catalyst (~3).

Thus, it was shown that the enhanced activity of the Ag/SBA catalysts in low-temperature CO oxidation may be achieved at optimal value of the SiOH/Ag ratio. However, the activity of the Ag/SBA-15 catalysts decreased with a growth of the Ag loading.

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# Selective catalytic hydrogenation for fine chemicals in micro capillary reactor

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Selective hydrogenation of the triple bond is an important class of chemical reactions for the production of pharmaceutical and perfume products. The main problem in this type of reaction is the control of the selectivity of hydrogenation and the decreasing the rate of the side hydrogenation of the double bond. In this work, the reaction of liquid-phase hydrogenation of the triple bond was investigated in a microcapillary reactor. This technology is advanced compared with the existing hydrogenation technologies, since it provides the environmental safety of the process, control of the contact time and the high rate of heat and mass transfer. Catalysts based on nanostructured oxide with embedded palladiumcontaining nanoparticles were synthesized as coatings on the inner surface of a microcapillary reactor. To develop methods for controlling activity and selectivity, the mechanism of the influence of the composition of the active component and support on the catalytic properties of embedded nanosized palladium-containing particles in the hydrogenation of 2-methyl-3-butyn-2-ol (MBY) was revealed.

The effect of particle composition is different for the colloidal and embedded particles, which were essentially determined by the geometric and electronic effects. Monometallic Pd colloid shows the highest activity and selectivity. An increase in the Pd:Zn ratio from 1 to 6 in the supported catalysts increased selectivity to alkene yield from 93% for the Pd catalyst to 95–96% for bimetallic catalysts, by decreasing the constants of the hydrogenation rate of 2-methyl-3-buten-2-ol (MBE) and the ratio of the alkene to alkyne and alkane adsorption constants [1].

Thermally stable catalytic coating for the selective hydrogenation of acetylene alcohols was prepared by doping Ce to titania matrix by the template sol–gel method. Investigation of the matrix with different amounts of Ce pointed out the important role of Ce in improving the thermal stability of the support by inhibiting the growth of anatase crystal [2]. The activity and selectivity of the thin coatings deposited onto inner surface of microcapillary reactor in a selective hydrogenation of MBY is strongly influenced by the support and nanoparticles composition. The highest activity was observed when using Ce-doped $TiO_2$ matrix with the activity sequence as: $Pd/(Ti,Ce)O_2 > Pd_{80}Zn_{20}/(Ti,Ce)O_2 > Pd/TiO_2$. The highest selectivity of MБE (94.2%) on Ce-doped coatings was obtained on the $Pd_{80}Zn_{20}/(Ti,Ce)O_2$ coating, which is higher by 14.5% than the yield in a batch reactor, was obtained in an atmosphere of hydrogen/helium mixture (H2/He = 1/1) at 313 K. The proposed kinetic model suitably describes the kinetics of MBY hydrogenation. A higher activity of Ce-doped catalysts and a higher yield of MBE over bimetallic catalyst under the same conditions were explained by decreased and increased adsorption constant of MBY, respectively. A higher activity of Ce-doped catalysts was explained by donation of electron density from $Ce^{3+}$ to Pd and weakening of the binding with alkyne.

This work provides fundamental information on the catalytic performance of the reaction in a microcapillary reactor and the promise of using this technology for liquid-phase hydrogenation of the triple bond was evaluated.

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# Supported catalysts containing δ-$MnO_2$ in low-temperature catalytic formaldehyde oxidation reaction

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HCHO removal from air attracts much attention due to the high toxicity and carcinogenic properties of formaldehyde. This process is utterly important for human health and environment protection. Formaldehyde sources are materials made from polyvinyl chloride, lacquered furniture, plastics based on phenol-formaldehyde resins, etc. Birnessite (δ-$MnO_2$) exhibits catalytic activity in low-temperature oxidation reactions of volatile organic compounds via the Mars - Van Krevelen mechanism. In contrast to α-, β- and γ-modifications, δ-$MnO_2$ possesses a layered structure consisting of two-dimensional sheets of $MnO_6$ octahedra with a basal interplanar distance of about 0.7 nm in which alkali metal ions $Li^+$, $Na^+$, $K^+$ and water molecules are intercalated [1]. Due to structural features and high reaction ability toward oxidative process, δ-$MnO_2$ is a good candidate for the development of catalyst composition used to eliminate formaldehyde from air at RT.

In the present work, manganese-containing catalysts with birnessite structure supported on silica gel and carbon materials were synthesized and studied.

$MnO_x$ over carbon material catalysts were prepared via hydrothermal method using an aqueous solution of $KMnO_4$. A silver-containing MnOx catalyst (5 % wt Ag) was prepared as follows. $AgNO_3$ solution was added to a solution of $KMnO_4$ immediately before the hydrothermal synthesis. $MnO_x$ supported on silica gel catalysts were prepared with the use of deposition-precipitation method [2], precipitation method [3], and redox reaction between oxalic acid and $KMnO_4$ on the surface of support [4]. The porosity, specific surface, phase composition and properties of the catalysts obtained were determined by low-temperature adsorption of nitrogen, Raman spectroscopy, X-ray phase analysis, TPx methods.

Testing of catalytic properties was carried out under the following conditions: temperature was 23-25 °C, flow rate was 300 ml / min, formaldehyde content in the gas flow was 60 - 90 ppm, catalyst mass was 0.0625 g. Analysis of inlet and outlet flows was performed by high-effective liquid-phase chromatography with using of DNPH formaldehyde derivatives.

Synthesized samples showed a degree of formaldehyde removal of about 90 % wt. from the gas flow. In the course of experiment the removal degree was reduced from 90 up to 20-30 % wt within 120 min. Among the tested samples, catalysts prepared with the use of carbon carriers and carbon-containing composites as supports were the most active and stable. It was a catalyst based on carbon material with a 14.8 % wt δ-$MnO_2$; carbon-based catalyst containing 49.8 % wt δ-$MnO_2$ and 2.4 % wt Ag; a catalyst based on silica gel with an inverted carbon structure containing δ-$MnO_2$ and silver similar to previous catalyst. After 120 min the degree of removal of formaldehyde from the gas flow was 35.3; 20.4; 15.5 % wt for the above-titled samples, respectively.

Decrease in the HCHO removal efficiency may be due to the formation of alkali metal carbonates stable on the catalyst surface at the experimental temperature and/or the low reoxidation ability at the reaction conditions. Subsequent studies will be devoted to identification of these factors as well as their elimination.

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# Tuning the selectivity of palladium catalysts in the synthesis of hydrogen peroxide by the anthraquinone method

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The report presents the results of studies of hydrogenation catalysts that allow purposefully changing the properties of palladium catalysts during the synthesis of hydrogen peroxide by the anthraquinone method. The main purpose of the anthraquinone process is the selective hydrogenation of 2-ethyl-9,10-anthraquinone (eAQ) to 2-ethyl-9,10-anthrahydroquinone ($eAQH_2$), which is readily oxidized by air oxygen to hydrogen peroxide with reduction of the initial substrate. However, the hydrogenation of alkylanthraquinones refers to complex series-parallel processes accompanied by side reactions. These include hydrogenation of phenyl rings and/or hydrogenolysis of the C-O bond in 2-ethyl-9,10-anthrahydroquinone. Testing of various catalysts in the hydrogenation of eAQ allowed us to formulate two diametrically opposed cases. Small palladium clusters 1.3-2.5 nm in diameter formed in Zigler-type systems, along with eAQ hydrogenation, exhibit high activity in the hydrogenation of the aromatic ring in $eAQH_2$. Star-like associates of palladium crystallites with a size of 127 ± 12 nm and a "branch width" of 18-20 nm accelerate mainly the hydrogenolysis of the C-O bond in 2-ethyl-9,10-anthrahydroquinone. Due to the side reactions, the selectivity of unmodified palladium catalysts in the selective hydrogenation of 2-ethyl-9,10-anthraquinone did not exceed 70%.

Modification of palladium catalysts with white phosphorus at the stage of their formation made it possible to increase the selectivity of Pd-P containing nanoparticles toward hydrogen peroxide from 69% (for Pd-black) to 96% (for Pd-P catalyst, P/Pd = 0.3). The reasons for the influence of the particle size and the modifying effect of phosphorus on the properties of palladium catalysts for the hydrogenation of alkylanthraquinones are considered, and also recommendations on the synthesis of catalysts for the hydrogenation of condensed aromatic compounds and hydrogenolysis of the C-O bond are proposed.

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# Study of nitrogen-doped carbon nanotubes as a promising support for heterogeneous catalyst for oxidation of organic substrates in the liquid-phase

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Nitrogen-doped carbon nanomaterials (N-CNMs) are of great interest for application in catalysis due to their exceptional physicochemical properties [1]. Doping of CNMs with nitrogen influences on acid-base, hydrophilic-hydrophobic and electro-physical characteristics of carbon nanomaterials. It was shown that use of N-CNMs as a catalyst support leads to the change of supported metal particles size, acceleration of electron transfer and formation of new adsorption sites on the carbon surface. Presently, different N-CNMs (nitrogen-doped carbon nanotubes (N-CNTs), carbon nanofibers, nanowires, nanorods, activated carbon, graphene) are successfully synthesized and studied for catalytic applications. The goal of the present work is to study the N-CNTs as a support for heterogeneous catalyst for oxidation of alkylphenols into benzoquinones in the liquid-phase.

CNTs were synthesized by catalytic decomposition of ethylene, whereas N-CNTs – by decomposition of 40% $C_2H_4$/60% $NH_3$ mixture on iron-based catalyst [2]. It was found that maximum nitrogen content in N-CNTs was 7,3 at.%. According to XPS data nitrogen is in 3 main electronic states: pyridinic, pyrrolic and graphite-like. TEM showed that CNTs have typical coaxial-cylindrical, whereas N-CNTs – bamboo-like structure. Doping with nitrogen increase the defectiveness and decrease of electrical conductivity of N-CNTs. It was explained by computer modeling by the use of the structure of g-$C_3N_4$ and turbostratic disordering.

For the first time polyoxometallate - divanadium-substituted γ-Keggin polyoxotungstate, $[\gamma\text{-}PW_{10}O_{38}V_2(\mu\text{-}O)(\mu\text{-}OH)]^{4-}$ ($V_2$-POM) was immobilized on N-CNTs. A series of supported catalysts $V_2$-POM/N-CNTs containing 5−25 wt % of $V_2$-POM and 0−7 at.% of N has been prepared and characterized by elemental analysis, $N_2$ adsorption, SEM, TEM, XPS, and FTIR techniques. It was shown, that the presence of nitrogen in the support ensures strong adsorption and molecular dispersion of V2-POM on the carbon surface.

The catalytic performance of $V_2$-POM/N-CNTs was assessed in the selective oxidation of 2,3,6-trimethylphenol (TMP) into trimethyl-*p*-benzoquinone. It was found that use N-CNTS with 1.8 at.% N as a support leads to high conversion and selectivity of catalyst. This catalyst does not suffer from metal leaching and can be used repeatedly without loss of the catalytic performance. Thus, it was shown that N-CNTs are a promising support for heterogeneous catalyst for oxidation of the organic substrates in the liquid phase.

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# Room temperature oxidation over mixed silver-nickel oxide $AgNiO_2$

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The search and development of new catalytic systems based on non-noble metals is an important investigation direction in the field of oxidative heterogeneous catalysis. One of the promising targets for catalytic oxidation can be mixed oxides of transition metals. Oxygen in the structure of mixed oxide is surrounded by different metal types that modify its electronic and reaction properties in comparison with single-metal-type oxide. Previously, the mixed silver-copper oxide $Ag_2Cu_2O_3$ demonstrated a great potential in CO oxidation at low temperatures [1, 2]. In this work mixed silver-nickel oxide $AgNiO_2$ was tested in the reactions of CO and $C_2H_4$ oxidation at room temperature.

Mixed oxide $AgNiO_2$ synthesized by co-precipitation in alkaline solution was characterized by delafossite-type layered structure. The crystallite size for pure $AgNiO_2$ was close to 2 nm. The analysis of structural diffraction data (XRD, PDF) revealed the presence of silver vacancies and stacking faults for the as-prepared $AgNiO_2$. The structure of mixed oxide in He or $O_2$ atmosphere was stable up to 350 °C, while the complete decomposition of $AgNiO_2$ under reaction conditions (CO- or $C_2H_4$-containing mixtures) occurred at 250 °C.

As-prepared $AgNiO_2$ demonstrated high activity in CO oxidation at room temperature with overall reaction rate of $7\cdot10^9$ $molecule\cdot sm^{-2}\cdot s^{-1}$. In case of partial $C_2H_4$ oxidation the activity of $AgNiO_2$ was also observed at room temperature (RT). The selectivity of $C_2H_4O$ formation was near 60-70 %. Although the activity in $C_2H_4$ oxidation at RT decreased during 40 min, catalytic measurements indicate the presence of weakly bounded oxygen species with high reaction probability towards CO and $C_2H_4$ on the surface of $AgNiO_2$. It was additionally confirmed by TPR-CO and TPR-$C_2H_4$ studies. Low-temperature $CO_2$ evolution for both TPR curves was observed in the region from 25 to 150 °C. The removal of reactive oxygen species from $AgNiO_2$ surface didn't result in mixed oxide structure destruction, while its slight modification was found.

XPS investigation revealed the simultaneous presence of $Ni^{2+}$ and $Ni^{3+}$ species and intermediate $Ag^0/Ag^{1+}$ silver state on the surface of the as-prepared $AgNiO_2$. XPS and XRF analyses confirmed the non-stoichiometry of as-prepared $Ag_{x<1}NiO_2$ with decreased Ag/Ni ratio, probably, due to the generation of silver vacancies. Interaction of $AgNiO_2$ with CO and $C_2H_4$ at 25-100 °C resulted in removal of two surface oxygen species with $E_b(O1s) = 529.0$ and 530.5 eV. Such species were attributed to lattice (Ag-O-Ni) and weakly charged ($O^-/OH^-$) oxygen forms, respectively. Also, the appearance of carbonate-like species with $E_b(O1s) = 531.5$ eV was found on the $AgNiO_2$ surface after the treatment with CO at RT, while in case of $C_2H_4$-containing mixtures similar species were formed only at heating up to 50-100 °C. The removal of active oxygen species was accompanied by slight decrease in Ag/Ni ratio and partial reduction of $Ni^{3+}$ to $Ni^{2+}$, while no changes in silver state were observed by XPS.

Based on all obtained data it was suggested, that reactive weakly charged oxygen species in form of hydroxyls can be allocated near silver vacancies within $AgNiO_2$ structure.

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# Influence of the preparation method of supported Fe-Mo-O/$SiO_2$ catalysts on their catalytic properties in selective oxidation of propylene glycol

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The processes of catalytic oxidation of organic substances are the sources of the most important compounds that are widely used in various industries. The selective vapor-phase oxidation of propylene glycol is a method for production of a number of available compounds such as hydroxyacetone (used in food and medical industries) [1], pyruvic acid (used in cosmetology) [2], methylglyoxal (used in medicine and food industry) [3, 4], etc. The catalysts based on oxides of transition metals, including iron and molybdenum (Fe-Mo-O), are widely used for the processes of selective oxidation of monoatomic alcohols. In industry, the Fe-Mo-O catalysts are used in the process of selective oxidation of methanol to formaldehyde [5]. The catalytic properties of supported Fe-Mo-O/$SiO_2$ catalysts in the process of selective oxidation of propylene glycol were not investigated.

The aim of the present work is to determine the influence of the order of introducing of the components (precursors of iron and molybdenum oxides) to the $SiO_2$ surface on the active surface state, the adsorption and catalytic properties of the supported Fe-Mo-O/$SiO_2$ catalysts in the selective oxidation of propylene glycol. The supported catalysts were prepared by the impregnation method without excess at Mo/Fe molar ratio of 1.5 and 3. The $MoO_3$ content was 10%wt. Spherical mesoporous silica gel grains were used as a support (Salavatsky catalyst plant, a specific surface was 300 $m^2/g$). For the $1.5Fe_2O_3/MoO_3/SiO_2$ and $3Fe_2O_3/MoO_3/SiO_2$ samples, the first stage included the impregnation of the support with a citric acid solution of ammonium heptamolybdate followed by drying at 100 °C and calcination at 600 °C. Then the catalyst sample was impregnated with a solution of iron (III) nitrate with the appropriate concentration. After each stage of sequential impregnation, the samples were dried and calcined in a stream of air at 600 °C for 4 h. The $MoO_3/Fe_2O_3/SiO_2$ samples with different Mo/Fe ratios were prepared using the reverse order of component introducing. The catalysts were investigated by electronic spectroscopy of diffuse reflection (DRS), Raman spectroscopy, TPR-$H_2$, XRD, low-temperature nitrogen adsorption, $TPR_x$ methods. According to the DRS data, the absorption bands at 300-450 and 450-600 nm characterized the samples prepared. According to the literature data, these bands corresponded to the absorption regions of $MoO_3$ and $Fe_2O_3$. The reaction ability of the catalyst surface was investigated by the TPR-$H_2$. The hydrogen consumption in the high-temperature region (550-620 °C) was typical for all samples. According to the literature data, the reduction of $Fe_2O_3$ proceeds at 350 °C. Molybdenum oxide inhibits the reduction of iron oxide, thus, a shift of the TPR peak towards the high temperature region was observed, which indicated the interaction between the two active phases.

The investigation of the catalytic properties showed that the highest selectivity towards methylglyoxal was observed for the $3MoO_3/Fe_2O_3/SiO_2$ sample (67 % at 360 °C). While the order of introduction of the active components onto the silica surface was varied, the significant redistribution of the reaction products occurred (the selectivity towards methylglyoxal decreased to up to 0%). The variation of the order of deposition of oxides for the samples with the Mo/Fe ratio of 1.5 showed negligible changes in the selectivity towards basic products. The catalytic properties of the materials prepared were compared with those for the supported $MoO_3/SiO_2$ and bulk Fe-Mo-O catalysts. The role of iron oxide in the formation of Mo-containing species on the catalyst surface is discussed.

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# The Investigation of NiMo/$WO_3$-$Al_2O_3$ Catalysts for Vegetable Oil Hydrodeoxygenation by Different EPR Techniques

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Electron paramagnetic resonance (EPR) spectroscopy is a convenient instrumental method, allowing to study paramagnetic species of functional materials (for example, carbon materials) or paramagnetic probes dynamics on the active surface. The method is very sensitive, nondestructive and can be used for the study of large samples series treated under the same condition.

Previously [1, 2] we've demonstrated some advantages of using probe EPR in the acidic properties investigation of NiMo/$WO_3$-$Al_2O_3$ (NiMo/WA-*x*, *x* = 0–30 % wt. of $WO_3$) catalysts and established few correlations with the catalytic properties in the vegetable oil hydrodeoxygenation reaction. Current work is aimed to the expanding of those researches by the application of probe or classical EPR not only for initial, but for deactivated and regenerated catalysts too.

All EPR measurements were carried out on Bruker EMXplus X-band (~9.7 GHz) spectrometer at 25°C. Each sample of initial NiMo/WA catalyst (synthesis and composition are reported in [1]) were thermally activated and treated by probe solution with further radical cations registration. The same approach was used for air-calcinated (regenerated) catalysts. As for deactivated catalysts, each one was placed directly into quartz tube and EPR spectrum was recorded without any treatment to characterize the surface carbon deposits (coke).

The EPR signal in deactivated catalyst is a typical spectrum of paramagnetic centers (PC) usually observed in carbon materials, and EPR spectra are similar for all the studied catalysts series. However, the integral intensities in the samples are different and depend on the concentration of PC in carbon deposits (coke). The spectrum is well described by the superposition of PC (defects) with g ~ 2.002 Lorenzian line, indicating the prevalence of delocalized or partially delocalized π-electrons in graphene layers of small length, as well as edge defects in layers related to the states of polarized electrons in the vicinity of the boundaries of zigzag shape [3] and possibly defects in $sp^3$-carbon bonds. It was also found that carbon deposits content (by thermogravimetric analysis – TGA) is related to the concentration of PC in each sample, thus EPR may be used as a fast method to evaluate the deactivation degree, caused by carbon (coke) deposition. It was also noted that the amount of carbon deposits (by TGA and EPR) correlates well with the concentration of acid sites determined by EPR with perylene probe. This fact can be an evidence of the determined acid cites predominant participation in the catalyst deactivation.

It was found by the probe EPR that the concentrations of perylene radical cations formed on the catalysts surfaces are close for both series – for the initial and regenerated catalysts, that indicates an almost complete removal of carbon deposits, as well as reset of its acid properties after oxidation regeneration.

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# Electronic properties of the active component of the Pd/γ-$Al_2O_3$ catalyst on a modified support

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Aluminum-palladium catalysts were synthesized and investigated. The γ-$Al_2O_3$ supports were obtained during the heat treatment of the modified pseudoboehmite ("Pural SB", Sasol). Modifiers were acetic acid, ammonium fluoride, sodium hydroxide and cesium nitrate. The number of acid sites was determined by the thermoprogrammed desorption of ammonia. For supports modified with acidic additives (acetic acid and ammonium fluoride) a decrease in the share of weak acid sites and an increase in very strong centers are observed compared with the unmodified sample. Samples of aluminum oxides containing sodium and cesium have a low acidity as a result of the suppression of strong acid centers.

The deposition of the active component was carried out from an organic solution of palladium acetylacetonate. Experimental curves were obtained from the results of the thermoprogrammed reduction by hydrogen. For all catalysts three regions of hydrogen evolution are observed. According to mass spectra the first two peaks are due to the reduction of palladium ions and the organic precursor ligand. The third peak corresponds to the complete reduction of the anions of the palladium salt. For catalysts based on supports modified with acidic additives, an increase in the intensity of the second peak and the total amount of absorbed hydrogen is observed. The deposition of a palladium salt to aluminum oxides treated with sodium and cesium compounds, on the contrary, is accompanied by a decrease in the intensity of hydrogen uptake in the average temperature interval, with simultaneous growth of the first low-temperature peak. Probably, hydrogen evolution in the second region occurs with particles of palladium in a more oxidized form.

The structural and electronic characteristics of the supported metallic particles were studied by chemisorption of CO, transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). The applied systems were subjected to preliminary treatment: oxidation with a mixture of 10 % $O_2$ in He at 400 °C (2 hours), holding for 10 minutes in He and subsequent reduction of 10 % $H_2$ in He at the same temperature for 2 hours. The size of the deposited metal particles was determined by chemisorption titration with CO. Calculation of the average diameter of metallic particles indicates approximately the same size, about 1.5 nm, which is confirmed by the TEM data. This allows us to assume that there is no manifestation of a "size effect" and to exclude its influence on the charge state of metal particles. Dispersion of the active component is more than 80%. The electronic state of the palladium particles was estimated by the XPS method. The palladium particles on an unmodified support are in the reduced (the content is 64 %) and oxidized (36 %) forms. The deposition of a palladium precursor to a support modified with acidic additives increases the proportion of oxidized particles to 75 %. The introduction of alkaline additives in the composition of aluminum oxides leads to an increase in the concentration of reduced palladium. Thus, for catalysts based on sodium and cesium containing supports, its fraction is 91 and 100 %, respectively.

Tests of the catalysts were carried out in the hydrogenation of 1.3-butadiene under incomplete conversion conditions at 35 °C in a flow-through reactor. Systems based on highly acidic supports are have low activity. For catalysts prepared using basic modifiers, high degrees of 1.3-butadiene conversion and selectivity to 1-butene are noted.

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# Gold catalysts for one-pot terpene alcohols amination

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One-pot alcohol amination proceeding through the hydrogen borrowing mechanism is an effective approach for production of valuable amines for fine chemicals synthesis and chemical industry in general. Biomass based amines are of great interest for development of new pharmaceuticals. Terpenoids belong to the largest group of natural compounds being extensively applied in food and perfumery industry as flavors, fragrances and spices. Utilization of natural terpenoids as platform molecules is of great interest for the synthesis of efficacious chemicals for human disease prevention and therapy [1]. The results of our previous work have shown that gold catalysts are rather active in one-pot amination of a natural terpene alcohol - myrtenol leading to predominant hydrogenation of C=N bond in the final step instead of a more reactive C=C group of myrtenol [2, 3]. The main objective of the present work was to study general regularities of one-pot natural monoterpene alcohol amination over gold catalysts as well as to determine correlations between catalytic activity, substrates structure, support nature and interactions of Au with other metals.

Liquid-phase monoterpene alcohol amination was carried out in a stainless-steel reactor. The reaction mixture was analyzed by GC, GC-MS and $^1$H- and $^{13}$C-NMR. A series of gold catalysts supported on metal oxides ($ZrO_2$, MgO, $Al_2O_3$, $CeO_2$, $La_2O_3$) were prepared by the deposition precipitation method, characterized by TEM, XPS, TPR/TPO-MS, pretreated under oxidizing or reducing atmosphere and finally tested in one-pot myrtenol amination. Catalytic activity and product distribution can be tuned by the metal oxide support properties, namely acidity and basicity, interactions of Au with other metals and the catalyst pretreatment conditions [2, 3]. Among the tested catalysts gold supported on $ZrO_2$ with both acidic and basic surface sites afforded the most efficient myrtenol transformations resulting in total conversion of myrtenol and selectivity to the target amine ca. 53 % [2]. The reaction kinetics was modeled based on the mechanistic considerations with the catalyst deactivation step introduced into the mechanism [4]. To improve selectivity to the desired product an effect on the reaction of external hydrogen sources, including molecular hydrogen, alcohols, formic acid, was studied [5, 6]. Application of 2-propanol allowed an increase of selectivity to the target amine with the maximum yield of 68 % being reached at the molar ratio of 2-propanol/myrtenol = 0.5 compared to 52 % in the absence of any additive. The substrates structures were also varied to obtain potential biological active compounds and to study their physiological properties. A noticeable effect of both alcohol and amine was demonstrated and explored [7]. A good correlation was found between the substrate structure and reactivity using the Hammett equation [7].

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# MoVNbTe oxide catalysts for ethane oxidative dehydrogenation: *in-situ* study of deactivation processes and influence of promoters

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Nowadays the industrial production of ethylene is based on the pyrolysis of the straight-run gasoline. This pyrolysis process has many sufficient drawbacks. Firstly, it is high energy consumption due to higher than 800 °C temperature, the usage of great amounts of water vapor, and endothermic character of C-C and C-H bonds breaking. The high temperatures leads to a loss decrease of selectivity due to various side reactions resulting in low yields of ethylene and a wide range of by-products. Oxidative dehydrogenation reaction to produce ethylene from ethane is a promising alternative. One of the most effective catalysts for low-temperature ethane and propane transformations are MoVNbTe oxide compositions [1, 2]. For instance, such catalysts demonstrate the ethylene yields up to 75 % in the oxidative dehydrogenation of ethane at temperature below 450 °C. It was shown that the catalytic activity of such catalysts in the oxidative dehydrogenation of ethane is determined by the amount of phase M1 [3]. The main drawback of such type catalyst for industrial application is instability under reaction conditions. The purpose of the present work was to investigate the stability of the M1 phase in different gas atmospheres and to understand the catalysts deactivation mechanism. The influence on this process of different promoters (P, Sb and Bi) was analyzed.

Catalytic properties of the samples in the oxidative dehydrogenation of ethane were studied in a flow setup Two composition of the starting reaction mixture were used: “standard” - $C_2H_6$:$O_2$:$N_2$ = 10:10:80 (vol.%) and “reducing” - $C_2H_6$:$O_2$:$N_2$ = 30:10:60 (vol.%) with the ratio $O_2/C_2H_6 = 0.33$, which is less than stoichiometric ratio for the selective conversion of ethane to ethylene.

The in-situ analysis of the structural stability of the catalysts was studied by the in situ X-ray diffraction (XRD) and the Near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) methods. The XRD data were obtained using Bruker D8 diffractometer (CuKα radiation) and Anton Paar XRK16 reaction chamber. The NAP-XPS experiments were carried out in the Charles University, Prague using a custom-built system (SPECS Surface Nano Analysis, GmbH Germany) equipped with a PHOIBOS 150 hemispherical energy analyzer, coupled with a differentially pumped electrostatic pre-lens system. The reaction NAP cell was installed in an analysis chamber that had a base pressure of ~10−10 mbar. The catalysts pre-treatment pressure was 10mbar and XPS studies were carried out at 1 mbar.

The obtained XRD data shows that the structure of the M1 phase is stable up to 550 °C in air and inert atmosphere (He), whereas it is completely destroyed in the $H_2$-containing (5 vol.% $H_2$ in He) atmosphere at 400 °C. The reduction by ethane or ethane-rich gas atmosphere is less destructive: the treatment at 460 °C results in appearance of the amorphous component and loss of the overall crystallinity of the samples. The NAP-XPS data shows that deactivation in the ethane-rich atmosphere results in significant decrease in Te/Mo ratio on the surface.

The addition of the Sb, P and Bi promoters influence both catalytic properties and stability of the catalysts. The loss of the ethylene yeld after deactivation grows in the following sequence for the studied promoters: Bi < P < MoVNbTeO < Sb, which indicates that Bi addition to the catalysts results in the best stability of the catalysts in the reductive atmospheres.

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# XPS analysis of $V_2$-POM immobilized on N-CNTs

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The use of carbon nanomaterials (CNMs) as supports for molecular and nanostructured catalysts is becoming a more and more popular strategy to improve heterogeneous catalysis. Many efforts have been devoted to doping of CNMs with heteroatoms as a way to tune the electronic, chemical and mechanical properties of the materials. Doping of the CNMs could provide new chemical groups on the surface beneficial for further functionalization of the materials in particular for immobilization of the active component of the catalysts in a dispersed state. In this regard, the method of X-ray photoelectron spectroscopy (XPS), which provides information on the surface composition and the charge states of the elements on the surface, is a powerful tool for analysis of the catalysts based on the carbon-nanomaterials.

In this work, we carried out the XPS study of nitrogen-doped carbon nanotubes (N-CNTs) with the variation of nitrogen content, as well as heterogeneous catalysts based on divanadium-substituted γ-Keggin polyoxotungstate, $[\gamma\text{-PW}_{10}O_{38}V_2(\mu\text{-O})(\mu\text{-OH})]^{4-}$ ($V_2$-POM), immobilized on N-CNTs. The XPS analysis of N-CNTs was carried out based on core-level spectra of carbon C1s, nitrogen N1s, and oxygen O1s. The charge states of the active component ($V_2$-POM) were followed by core-level spectra of vanadium V2p, tungsten W4f, and phosphorus P2p. The XPS analysis of the unsupported $V_2$-POM was performed to collect reference data.

The XPS analysis of N-CNTs with nitrogen content (0-4.8 at% N) revealed three main types of nitrogen species which based on the values of binding energy ($E_b$) were be attributed to pyridine-like ($E_b$(N1s)= 398.3–398.5 eV), pyrrole-like ($E_b$(N1s)= 399.6–400.2 eV), and graphite-like nitrogen ($E_b$(N1s)= 400.8–401.3 eV). The oxidized state of nitrogen and molecular nitrogen encapsulated inside N-CNTs were also observed with $E_b$(N1s)~403 eV and $E_b$(N1s)~405 eV, respectively. The impact of pyridine-like nitrogen increased with increasing the total N content and reached ~26% in N-CNTs with 4.8 at% of N.

The XPS analysis of $V_2$-POM sample showed that the charge states of the elements corresponded to the oxidation states of the elements in the $V_2$-POM structure. The tungsten spectrum W4f can be described with one main 4f doublet with $E_b(W4f_{7/2})$=35.5 eV typical of the $W^{6+}$ oxidized state. The maximum of the vanadium $V2p_{3/2}$ peak is characterized by a binding energy of 517.2 eV related to the vanadium $V^{5+}$ oxidized state. The immobilization of $V_2$-POM on the N-CNT surface did not lead to noticeable changes in the charge states of the elements of the active component or support. Thus, XPS analysis indicated the stability of the $V_2$-POM structure after immobilization on the N-CNTs surface. TEM data showed that single polyanions were attached to the surface of N-CNTs, whereas aggregation of $V_2$-POM species was observed for nitrogen-free CNTs.

Substantial changes were observed in the quantitative ratio of the elements on the surface. There was a significant increase in the V/W ratio after $V_2$-POM immobilization on the surface of N-CNTs. For the $V_2$-POM/N-CNTs sample, the V/W ratio increased by a factor of 1.5 in comparison with $V_2$-POM sample. Such changes might be related to the specificity of $V_2$-POM immobilization on the surface of N-CNTs. Since XPS is a surface-sensitive technique, the elements on the surface give the highest impact to the overall spectrum. A significant increase in the amount of vanadium observed in the XPS spectra of $V_2$-POM/N-CNTs sample might indicate the stabilization of $V_2$-POM molecules through oxygen groups of tungsten with $\{V_2(\mu\text{-O})(\mu\text{-OH})\}$ core oriented opposite to the surface of N-CNTs.

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# Preparation and catalytic activity of lanthanide-grafted Nafion/CNF composites

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Perfluoroalkanesulfonate metal salts were successfully used in a number of homogeneous processes of fine organic synthesis traditionally catalyzed by Lewis acids, such as $AlCl_3$, $BF_3$ etc [1]. An important advantage of such salts in comparison with standard Lewis acids is their stability in proton media and ability to catalytic recycle. These studies developed in various works, for example: (i) lanthanide triflates supported on silica [2], (ii) lanthanides contained in polystyrene stabilized microemulsions [3], (iii) grafted to sulfonated fluoropolymer (Ln-Nafion) and to acidic resins (Ln-Amberlyst etc.) [4]. All these systems possesses mentioned ability to use protic media while maintaining efficiency in the catalytic cycle. This work is a step forward from pure Ln-Nafion systems to the carbon nanofibers (CNF) supported Ln-Nafion systems. Rationale behind that decision is the desire to reduce the weight of Nafion (Nf) used, while maintaining catalytic activity, due to increased availability of sulfonic groups. High texture characteristics of the Nf/CNF [5] samples have also great impact on the catalytic process. Various supported Ln-Nf catalysts are synthesized (Ln = Yb, Tm, Pr, Eu, La) and tested in ethanol acylation reaction with acetic acid, and in catalytic acylation over a wide range of alcohols.

The $Ln^+$-grafted composites were synthesized by ion-exchanging of Na-precursor ($Na^+SO_3^-$ Nf/support or $Na^+SO_3$CNF) with excess (1:100 mol: mol) of $LnX_3$ aqueous solution (X = Cl, OAc; Ln = Sc, La, Pr, Eu, Tm, Yb). Lanthanide cation content in resulted ion-exchange sample was defined by AAS-analysis. The structure of the synthesized samples was investigated by the set of methods: electron microscopy, BET, SAXS and XPS. In typical experiment, the catalytic activity of Ln-grafted composites was tested in an ethanol etherification model reaction. $Ln^+$composite (1 g) was added to stirred mixture of ethanol (99.9 wt. %, 3 M) and acetic acid (99.7%, 6 M) in 45 ml of THF.

In summary the highest initial rates were realized when acylation catalyzed by $H^+$-acid samples (without metals, $H^+$Nf/CNF and $H^+SO_3$-CNF). However, the product yield was low due to equilibration of EtOH acylation and of EtOAc hydrolysis. In the lanthanide screening test the highest catalytic activity was shown for the samples contain of Yb or Sc (Sc~Yb>Tm>Eu>Pr>La). Similar activity rows are inherent for other acid catalytic reactions (e.g. nitration over $Ln(OTf)_3$). This may be explained by the decrease of ion radius (while increasing the cation charge density) in that row. Catalytic systems of the composition $Ln^{3+}$-Nf/CNF have a higher catalytic activity than the $Ln^{3+}$-$SO_3$-CNF systems. The higher acceptor properties of the -$SO_3$-$CF_2$- Nafion groups provide a greater lanthanide cation charge density. In the case of acylation a wide range substrates (secondary and tertiary alcohols) by acetic acid catalytic activity decreased. This is presumably associated with steric hindrance. The active cites of prepared systems are lanthanide cations grafted to Nafion sulfonic groups. The substrates presumably polarize on the lanthanide cation while the esterification reaction.

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# Effect of Se doping on the properties of MoVTeNbO catalysts for ethane oxidative conversion to ethylene

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Industrial processing of associated petroleum gases and its components - methane, ethane and propane is in the focus of both fundamental and applied research. Oxidative dehydrogenation of ethane (ODE) is regarded as perspective alternative to industrial steam cracking process for ethylene production. To date, the MoVTeNbO is one of the most effective catalytic systems for ODE [1, 2]. The catalytic activity and selectivity of such catalysts are attributed to the so-called M1 phase.

The synthesis of M1 phase via 'slurry' method is a non-equilibrium process, where the chemical composition is a crucial factor that influences the phase composition of the final catalysts. For instance, the presence of Te in the initial slurry results in the formation of the M1 phase after thermal treatment of the spry-dried slurry in He. The effect of Te is explained by the stabilization of big hexagonal channels in the M1 structure. Se is the chemical analog of Te. It can also promote the formation of the M1 structure. The goal of the present work was to study the effect of Se promotion on the formation process of the M1 phase in the MoVTeNbO mixed oxide catalysts for oxidative dehydrogenation of ethane to ethylene.

$Mo_1V_{0.3}Te_{0.23}Nb_{0.12}Se_{0-0.15}$ catalysts were synthesized from aqueous slurry according to the procedure described in [3] using ammonium heptamolybdate, ammonium metavanadate, telluric acid, selenious acid and makeup solution of niobium oxalate. As prepared crude precursors were fast dried at 220ºC and calcined stepwise in air flow at 310°C shortly and then in He flow at 350-550°C for 2 h. The samples were characterized by XRD, XPS, BET and atomic absorption spectroscopy methods. The ethane oxidative dehydrogenation was carried out in a fixed-bed tubular reactor with on-line chromatographic analysis of the reaction mixture components. Experiments were performed at atmospheric pressure and temperature 400ºC using feed consisted of a mixture $C_2H_6$: $O_2$:$N_2$ = 10:10:80 (% об.).

XRD, EDX and element analysis show that Se is completely removed from the catalysts after heating in He at 550°C independently on the initial concentration in the precursor. However, Se was detected in the composition of the catalysts after heating up to 450°C. In the spray-dried precursor, the surface concentration of Se corresponded to the bulk concentration. It indicates the homogeneous Se distribution in the sample at the first stage of synthesis. The heating in air at 310°C and subsequent heating in He flow at 310-450°C reduced the Se concentration by 25 times compared with initial concentration. The heating above 450°C resulted in the complete Se loss from the catalyst. The M1 and M2 phases were detected in the catalysts after heating at 550°C. The content of the M1 phase was varied from 85 to 93 weight % for the samples with different given Se content. The crystallinity degree was 80-93%, which exceeded the crystallinity degree of the standard catalysts without Se obtained by the similar synthesis procedure.

The obtained catalysts showed higher activity in ODE and higher ethylene selectivity then standard MoVTeNbO catalysts obtained without Se addition. The obtained difference can be attributed to better crystallinity of the M1 phase obtained in the Se-promoted samples. Se might promote the crystallization of the M1 structure from the initial mixture. Se loss during the catalysts heating also might promote the formation of more active oxygen species, similarly to Te los, as it was shown in the ref. [4].

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# Features of morphology and acid-base properties of the surface, and luminescent characteristics of synthesized phosphors $YPO_4$:Eu, $YVO_4$:Eu, $YVPO_4$:Eu

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The compounds of rare-earth elements attract the attention of researchers in connection with their wide practical application. Inorganic materials based on complex oxide compounds are widely used as adsorbents, catalysts, phosphors.

The development of novel synthetic approaches to oxide phosphors with high luminescence efficiency is one of the most important steps towards obtaining various high-tech devices, including plasma panels, auto-electron emission displays, light sources of a new generation, thermoluminescent dosimeters, etc. The application in such devices determines specific requirements to functional properties of the relating luminescent materials, particularly involving a high quantum yield of luminescence and presence of certain absorption and emission bands.

There are a large number of compounds doped with rare-earth ions, the most attractive of which are the oxides of these ions [1-4]. Most of them have thermal stability, as well as good chemical activity. Such compounds include phosphors based on vanadate and yttrium phosphate, activated by europium.

The aim of this research is to synthesis of the phosphors activated by europium namely yttrium vanadate, yttrium phosphate and their combinations as well as determination of the relationship between morphological and acid-base properties of their surface, and luminescent characteristics of this materials.

A series of $YPO_4$:Eu, $YVO_4$:Eu and $YVPO_4$:Eu phosphors with different content of Eu(III) activator and with different phosphorus-vanadium ratio for the mixed phosphors are synthesized by the SHS method. It is shown by the SEM method that all the elements, including europium activator, are homogeneously distributed on the particles surface with the dispersion, the porosity, and the value of the specific surface of the phosphors being different [5]. The most finely dispersed samples are $YVO_4$:Eu and mixed samples. Specific surfaces_of finely mesoporous $YPO_4$:Eu are 10-15 times higher than vanadate and mixed samples. pH-metry and the indicator method show that the investigated phosphors have a slightly alkaline ($YVO_4$:Eu, $YVPO_4$:Eu) or slightly acid ($YPO_4$:Eu) state of the surface with different content of Lewis and Brönsted sites. It is found that the differences in the functional composition, acid-base state of the phosphor surface, along with other factors, cause a difference in the intensity and brightness of the photoluminescence (PL) of the investigated phosphors [6]. The possibility of synthesizing yttrium-phosphate-vanadate phosphors of mixed $YV_xP_{1-x}O_4$:Eu composition with increased brightness and PL intensity compared with phosphate and comparable with vanadate phosphors is demonstrated. Phosphors of mixed composition become more effective in combination with greater availability and lower cost, compared to phosphors based on yttrium vanadate.

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# Development, synthesis and investigation of titania-zirconia nanomaterials for application in microcapillary reactors

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Ordered mesoporous titania-zirconia $Ti_xZr_{1-x}O_2$ composites were synthesized by self-assembly using titanium isopropoxide and zirconium oxychloride as precursors and amphilic triblock copolymer F127 as a template [1]. The self-assembly process proceeds without the addition of acid, which is necessary to preserve the morphology and structure of the catalytic nanoparticles. A number of samples were prepared by varying the Ti content from 0 to 100% (designated as 0Ti, 15Ti, 30Ti, 70Ti, 100Ti). In the low angles region, a peak near $1.63^0$ is observed in diffractograms, indicating ordered structure of pores. According to high angle X-ray diffraction data, the anatase phase peaks (JCPDS 71-1169) are present in pure $TiO_2$. Increasing Zr content inhibits crystallization, since the samples of 15 Ti, 30Ti, and 70Ti are in an amorphous state. Samples with high Zr content contain mainly the tetragonal phase of $ZrO_2$ (JCPDS 17-0923) and traces of the monoclinic $ZrO_2$ phase (JCPDS 37-1484). After oxidative treatment at 600 °C, the mesostructure of 70Ti is destroyed, while the mesostructures of samples with a higher Zr content are retained (30Ti and 15Ti). In the high angles diffractograms the sample 15Ti after oxidation at 600 °C contains the orthorhombic phase $ZrO_2$ (JCPDS 34-1084); the sample 70Ti contains the phases $Ti_2Zr_2O_6$ (JCPDS 46-1265) and $Ti_7Zr_5O_{24}$ (JCPDS 34-209); the sample 30Ti is amorphous. When the temperature is increased to 600 °C, the peaks become narrower and more intense. For samples 15Ti and 70Ti, the crystallite size increases from 1.4 nm to 17 nm and from 1.2 nm to 17 nm, respectively. The growth and increase in the size of crystallites leads to the destruction of mesostructures. For the 30Ti sample, this change is less pronounced, with the particle size calculated by the Scherrer equation increasing from 1.3 to 1.5 nm. After calcination at 800 °C, the pore walls crystallize to $ZrTiO_4$ (JCPDS 34-0415). It is obvious that crystallization leads to the destruction of the mesoporous structure due to the phase transformation and the rapid growth of nanocrystallites. The structure of pore walls and their thermal stability are systematically studied by transmission electron microscopy and low-temperature adsorption of nitrogen. Composites possess an ordered pore mesostructure, a high specific surface area (up to 157 $m^2/g$), a large pore volume (0.13-0.21 $cm^3/g$), and a uniform pore size distribution (3.6-3.7 nm). This approach can be used to develop an ordered mesoporous catalytic coating for use in microcapillary reactor.

The coatings of 1.7 wt.% $PdZn/TiO_2$ and 1.4 wt.% $PdZn/Ti_{0.8}Zr_{0.2}O_2$ (molar ratio Pd/Zn 1/1) on the inner surface of a capillary reactor 0.53 mm in diameter, 10 m in length were synthesized. The coatings were tested in selective hydrogenation of 2-methyl-3-butyn-2-ol at 333 K and 1 atm $H_2$. The yield of the product of 2-methyl-3-buten-2-ol was 3.6 and 5.8 g/day, selectivity was 97.1 and 97.2% at 98% conversion on $PdZn/TiO_2$ and $PdZn/Ti_{0.8}Zr_{0.2}O_2$ coatings, respectively.

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# Design of Ag-CeO$_2$ catalysts with strong metal-support interaction for selective reduction of nitroarenes into corresponding amines

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The selective reduction of nitroarenes to corresponding amines is of great importance, because amines are an important precursor for the synthesis of dyes, pesticides and pharmacological preparations in chemical industry [1]. The development of more active, selective and eco-friendly catalysts, as well as ways to carry out amine synthesis in mild conditions, is important for both basic researches and for industrial applications. The aim of this work was to synthesize and study CeO$_2$-based catalysts for the selective reduction of nitro compounds.

Series of Ag-CeO$_2$ catalysts with molar ration Ag:Ce=2:8 were prepared by two techniques: co-precipitation of Ce(NO$_3$)$_3$ and AgNO$_3$ by aqueous ammonia solution [2] (samples Ag-CeO$_2$-1 and Ag-CeO$_2$-2) and incipient wetness impregnation of ceria by aqueous solution of AgNO$_3$ [3] (sample Ag/CeO$_2$). Then, samples were dried at 120 °C of 2,5 h and calcined in air flow at 500 °C of 4 h. Catalysts were characterized by low-temperature N$_2$ adsorption, TPR, UV-vis spectroscopy and tested in reaction of reduction of nitrophenol by NaBH$_4$ in aqueous solution at room temperature and atmospheric pressure.

According to low-temperature N$_2$ adsorption data, isotherms of N$_2$ adsorption-desorption for all samples are characterized by the hysteresis loop, which indicates on the mesoporous structure of catalysts. CeO$_2$ is characterized by a specific surface area of 28 m$^2$/g and pores of 2-30 nm. The Ag/CeO$_2$ specific surface has 11 m$^2$/g and pores of 5-30 nm, which indicates the distribution of silver mainly in shallow pores of the support. A significant decrease in the specific surface area for catalysts is due to the high silver content of 20 % mol. The sample of Ag-CeO$_2$_2 has a specific surface area of only 5 m$^2$/g, which may be due to the most complete oxidation-reduction reaction between Ag$^+$ and Ce$^{3+}$ ions in the solution during the deposition stage in an alkaline medium.

The features of reduction of catalysts were studied by the method of temperature-programmed reduction by hydrogen (TPR H$_2$). The reduction of CeO$_2$ is characterized by the presence of two temperature regions: peak at 700-900 °C is associated with the reduction of the volume of CeO$_2$ particles, while peak at 220-600°C may be attributed with the reduction of the surface of the CeO$_2$ particles. For Ag-containing catalysts low temperature H$_2$ consumption at 100-150°C mainly may be associated with reduction of AgO$_x$ species. However, disappearance of peak at 300-600 °C of reduction of surface CeO$_2$ indicates on simultaneous reduction of AgO$_x$ species and surface CeO$_2$ at 150-200 °C. Increased intensity of this peak for catalysts, prepared by co-precipitation indicates on the strong interaction between active component and CeO$_2$ particles.

The catalytic properties of the catalysts were studied in the reduction reaction of n-nitrophenol with sodium borohydride (NaBH$_4$) at room temperature and atmospheric pressure. CeO$_2$ does not catalyze the reduction of 4-nitrophenol. The introduction of silver into the catalyst promotes the reaction. Thus, on the Ag/CeO$_2$ catalyst, the reduction of p-nitrophenol proceeds in 15 minutes, and ones over the catalysts prepared by the co-precipitation method was 9-12 min. Thus, Ag-CeO$_2$_1 and Ag-CeO$_2$_2 are more active in this reaction that we attribute with stronger metal-support interaction in these catalysts.

Thus, it was shown that the method of catalyst preparation (impregnation and precipitation) affects the structures of the formed Ag-CeO$_2$ catalysts and metal-support interaction. This interaction affects the oxidation-reduction properties of the catalyst and catalytic activity in the selective reduction of nitrophenol in mild conditions.

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# Fourier transform infrared spectroscopic imaging is an advanced method for studying the aggregation of crude oil components

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IR spectroscopy is a classical method for analyzing the chemical composition of a wide range of materials, as well as studying the mechanisms of chemical reactions. The use of the Focal Plane Array increases the capabilities of IR spectroscopy, allowing the study of the material with spatial resolution, thus obtaining the so-called "chemical imaging". An array detector produces a two-dimensional picture, in which each point is correlated with the integrated absorbance of a characteristic IR band measured for a local site of the surface. FTIR spectroscopy imaging makes it possible to investigate the dynamic processes of diffusion, precipitation, isotopic exchange [1], and chemical reactions in the flow regime [2]. The attenuated total reflection (ATR) mode in combination with the FTIR spectroscopy imaging [3] allows carrying out studies of dynamic processes at high temperatures and pressures [4].

More recently, the method of FTIR spectroscopy imaging has been applied to study the formation of deposits in the real equipment used for petroleum refining [5] and it has been shown that different functional groups (carbonates, sulfates, esters) have a certain spatial distribution. It is known that asphaltenes are one of the main components of heavy oils that play a key role in the formation of sediments. Asphaltenes are prone to self-association and the formation of aggregates, which under certain conditions can lead to their irreversible flocculation and sedimentation. The method of FTIR spectroscopy imaging was applied to the study of the loss of phase stability of asphaltenes with the addition of flocculant [6], when mixing different types of crude oils [7] and crude oil-$CO_2$ systems [8]. It has been shown that functional groups with different heteroatoms (oxygen, nitrogen and sulfur) play a key role in the aggregation of asplftene.

In continuation of FTIR spectroscopy imaging was used to study the precipitation of asphaltenes in the flow conditions flocculant (heptane). The experiment was carried out in microfluidic devices filled with a solution of asphaltene in benzene. The maps of distribution of the main components of a model mixture of heptane, benzene and asphaltenes were obtained depending on the duration of the experiment. Analysis of the chemical composition of the obtained asphaltene precipitation showed that the precipitates have a spatial heterogeneity in the ratio of $CH_3/CH_2$ groups in the direction of the flocculant flow and the conditions for the formation of the precipitate.

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# Phenothiazine as a spin-probe for testing electron-acceptor sites on the surface of oxide catalysts

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Spontaneous ionization of aromatic molecules is known since the 1960s. The presence of active surface sites of different strength, capable of ionizing the aromatic molecules has been suggested. Electron-acceptor sites of different strength can be characterized using aromatic probes with different ionization potentials [1, 2]. Our recent results suggest that such sites are most likely responsible for decomposition of halocarbons [3,4] and ethanol dehydration [5]. This study was devoted to analysis of relations between the concentrations of electron-acceptor sites and modifying components and mechanisms of processes taking place on different sites and adsorption aromatic molecules.

Phenothiazine ($C_{12}H_9NS$) is an aromatic molecule with a very low ionization potential (6,8 eV) that allows testing weaker electron-acceptor sites on the surface of catalysts than antracene (7,4 eV) and perylene (7,0 eV) used more often. Its EPR spectrum is characterized by hyperfine splitting constant on the nitrogen atom about 14-16 G depending on the nature of the studied sample.

The aim of this study was to investigate possibility of using phenothiazine for testing electron-acceptor sites on the surface of different oxides at different temperatures. A technique developed by us for other spin-probes was used [2]. The sample was activated in air at desired temperature for 3 hours, then cooled down to room temperature and filled with a spin-probe solution ($2\times10^{-2}$ mol/l in toluene). EPR spectra were registered immediately after spin-probe adsorption and after heating at 80 °C for 18 hours. Such heating allows measuring the concentration of the weakest sites tested with this probe.

Properties of spin probes were studied using a model system of $\gamma$-$Al_2O_3$ with different concentrations of doped sulfates (0, 2, 4, 8, 12, 16 wt. %). Electron-acceptor sites tested with phenothiazine immediately after adsorption, i. e. corresponding to its ionization potential, are present on all the samples of the model system, including pure $\gamma$-$Al_2O_3$. Their concentration increases with the increase of doped sulfates amount till 8 wt. %, then slightly decreases for samples with higher sulfate content. The concentration of the weakest electron-acceptor sites tested after heating at 80°C for 18 hours increases on all the samples with increasing the concentrations of deposited sulfates. Overall, concentrations of the sites tested with phenothiazine are significantly higher than those obtained with perylene. For example, on the surface of the sample containing 8 wt. % of doped sulfates, the concentration of electron-acceptor sites measured using perylene after heating at 80°C is $2,3\times10^{19}$ $g^{-1}$, while the one measured with phenothiazine is $5,7\times10^{19}$ $g^{-1}$. It is also shown that sites revealed using phenothiazine exist on all samples activated at 150-300 °C. On the samples with high amounts of sulfates some sites are observed even without activation.

In addition, electron-acceptor sites were tested with phenothiazine on several other oxides used in catalysis. Their presence was shown on all the studied samples, including nanocrystalline MgO, where no sites capable of ionizing perylene were observed. Thus, phenothiazine appears to be a promising spin-probe for testing the weakest acceptor sites of oxide catalysts.

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# Effect of Mo:V ratio on surface phase composition and catalytic characteristics of $V_2O_5$-$MoO_3/Al_2O_3$ catalysts for oxidative dehydrogenation of propane

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Supported vanadia composites are known as promising catalysts for oxidative dehydrogenation (ODH) of light alkanes including propane. A high catalytic performance of such catalysts is caursed by the distribution of vanadium over the support surface in the form of 2D vanadia species. However, a low selectivity due to propylene overoxidation remains a challenge. Modification of vanadia catalysts with oxides of various metals (such as Mg, Mo, etc.) was shown to contribute to the increase of selectivity towards the target product.[1-2] At the same time, the optimal composition and structure of the active species in the multicomponent systems as well as their relationship with the catalytic properties remains unclear. In our previous work, the features of the formation of active species in the supported monolayer $V_2O_5$–$MoO_3/Al_2O_3$ catalysts for ODH of propane depending on the preparation approach were studied, with the consecutive impregnation of alumina support firstly with the solution of vanadium precursor and secondly with the solution of molybdenum precursor being the most advantageous. The present work is focused on the study of the effect of the active components ratio in the monolayer $V_2O_5$-$MoO_3/Al_2O_3$ catalysts on their catalytic properties towards propane ODH.

A series of $V_2O_5$-$MoO_3/Al_2O_3$ catalysts with a total V + Mo content corresponding to the monolayer surface coverage and different V : Mo ratio were prepared by the consecutive support impregnation of alumina support firstly with the solution of vanadium precursor and secondly with the solution of molybdenum precursor. Ammonium metavanadate $NH_4VO_3$ and ammonium heptamolybdate $(NH_4)_6Mo_7O_{24}$ were used as starting compounds of the supported components. To increase the solubility of $NH_4VO_3$ and $(NH_4)_6Mo_7O_{24}$, oxalic and citric acids were used, respectively. The vanadium content in the $V_2O_5$-$MoO_3/Al_2O_3$ catalysts prepared was 0.15, 0.3, 0.5, and 1 monolayer. The intermediate $V_2O_5/Al_2O_3$ and $V_2O_5$-$MoO_3/Al_2O_3$ target samples were calcined at 500 ºC. A complex of methods including low-temperature nitrogen adsorption, UV-vis DR and Raman spectroscopy was used to study the textural characteristics, phase composition and structural characteristics of the obtained samples. The catalytic properties of the samples were studied in the reaction of oxidative dehydrogenation of propane.

According to UV-vis DR and Raman spectroscopy, the supported components are present in samples in the form of surface oligomeric or polymeric $VO_x$ and $MoO_x$ species, with V-O-Mo bonds being formed at the interfaces of the species. The effect of composition and structural features of the surface species formed in $V_2O_5$–$MoO_3/Al_2O_3$ catalysts on their catalytic properties are considered in details.

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# Structural and catalytic properties of $V_2O_5$-$La_2O_3$/$SiO_2$ catalysts

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Supported vanadium oxide catalysts are known as catalysts for various oxidative reactions such as oxidative dehydrogenation of light hydrocarbons, oxidation of formaldehyde, methanol and ethanol, etc. [1]. Catalytic properties of such catalysts are caursed by the presence of vanadium in the form of two-dimensional surface $VO_x$ phases, with their structure and reactivity being depended on the support nature. The support influences on both the surface density of two-dimensional $VO_x$ phases and their reactivity. Silica is one of the widely used inert support, characterized by a specific surface area and porosity controlled in a wide range [2]. However, it suffers from formation of the three-dimensional vanadium oxide particles possessing low selectivity towards target products at significantly low vanadium loadings. The support modification allows enhancing the surface density of two-dimensional metal oxide species as well as changing the redox potential of vanadium oxide species. The present work is focused on the study of the surface phase composition, structural features, redox characteristics, and catalytic properties of the $V_2O_5$-$La_2O_3$-$SiO_2$ catalysts.

Supported vanadium catalysts were synthesized by consecutive and cooperative incipient wetness impregnation of silica with lanthanum nitrate and vanadyl sulfate solutions. The samples prepared were studied by a complex of methods, including low-temperature adsorption by nitrogen, IR and Raman spectroscopy, TPR-$H_2$, UV-vis DR spectroscopy. Catalytic properties were studied in the oxidative dehydrogenation of propane.

The composition and structure of the surface phases in the supported $La_2O_3$-$V_2O_5$/$SiO_2$ samples were shown to depend on the approach of introduction of supported component. The introduction of vanadium oxide to silica support modified with lanthanum oxide results in formation of surface two-dimensional $LaVO_x$ species with different number of lanthanum atoms in the second coordination sphere of vanadium. Modification of the $V_2O_5$/$SiO_2$ sample by lanthanum oxide as well as co-impregnation of silica with both V and La precursors results in the formation of a mixture of microcrystalline lanthanum orthovanadate and $V_2O_5$. The formation of two-dimensional $LaVO_x$ species on the silica surface was shown to provide both high activity and selectivity of the $V_2O_5$-$La_2O_3$/$SiO_2$ sample.

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# The Features of 1,3,5-trinitrobenzene Application as a Probe for Basic Sites on the Different Thermally Treated MgAl-layered Double Hydroxides Studied by EPR Spectroscopy

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Layered double hydroxides (LDHs) are widely used as adsorbents, supports and catalysts of basic type [1]. The important advantage of such systems is the possibility of adjusting their basic properties by modifying with different cations, or during the activation procedure. This fact is due to the layered structure of these materials and significantly affects on their adsorption and catalytic properties.

In current research the basic properties of MgAl-layered double hydroxides series with different Mg:Al atomic ratio (LDH-MgAl-*Y*, where *Y* is the Mg:Al atomic ratio = 2.2, 3.1 and 4.2) were investigated by probe EPR. The EPR measurements were carried out on Bruker EMXplus X-band (~9.7 GHz) spectrometer at 25°C. Each sample of LDHs was activated at 150, 300 or 550°C and treated by 1,3,5-trinitrobenzene (TNB) solution in toluene or n-hexane with further registration of EPR spectra. Pristine $\gamma$-$Al_2O_3$ was used as a comparison sample.

Mono-, di-, and trinitroaromatic compounds may form anion-radicals during the adsorption on the surface of metal-oxide systems. This phenomenon was first observed by EPR for alumina [2] and magnesia [3]. The subsequent development and systematization [4] of the data allowed explain the formation of paramagnetic product by the interaction of the donor (basic) surface sites and nitroaromatic probe molecules. It led to the discussions of the possibility of using nitroaromatics in the surface basic sites study. Nevertheless, the influence of many aspects (solvent, probe concentration, oxide activation conditions, etc.) is not fully understood. In fact, there are no such data for LDHs.

Throughout the entire activation temperature range (300-550°C) the differences in the formed TNB anion-radicals concentration for LDHs and alumina are negligible, the values are $1–5 \times 10^{17}$ spin/g at 300°C and $1.5–2 \times 10^{18}$ spin/g at 550°C. It's obvious, that at a higher activation temperature more active sites become available for probe due to the removal of surface (or interlayer) water. At the same time, the close basicity values of LDHs and alumina do not mean their similar properties, since alumina has a large number of acidic sites along with the basic sites. This is clearly seen in the EPR spectra of TNB adsorbed on alumina from hexane: the signal is broadened, which is probably due to the migration of the nitroxide-like nitroaromatic anion-radicals to the BAS and LAS of the surface. We suppose that this fact plays an important role in stabilization of the produced paramagnetic particles. The LDHs spectra for the series is represented by a triplet with parameters: $g_{iso} = 2.004$, $A_{xx} = 5.5$ G, $A_{yy} = 2.5$ G, $A_{zz} = 28.5$ G, $B_{iso} = 9.0$ G. Unlike hexane, in toluene all spectra look similar, so it's impossible to detect the interaction of the probe with acid sites. This is probably due to the competitive adsorption of TNB excess, connected to its higher solubility in toluene. Thus, n-hexane seems to us a more preferable solvent in the study of the alumina and LDH-MgAl-*Y* basic sites.

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# The study of Cr–Zr oxide catalysts for propane dehydrogenation

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Catalytic dehydrogenation of saturated hydrocarbon is one of the main industrial processes. The dehydrogenation products (propylene, isobutylene etc.) are used to synthesize important chemical compounds and polymers [1]. Catalysts that contain $CrO_x$ or Pt–Sn as the active component are the main types of industrial catalysts for the dehydrogenation of $C_3$-$C_5$ alkanes. However, platinum is an expensive metal, while some chromium compounds are toxic. Alternative systems still remain less active than the industrial catalysts. The development of a catalyst with a low content of chromium oxides, which have high activity in dehydrogenation of saturated hydrocarbons, is an actual task due to the requirement of environmental safety and energy efficiency of industry [1, 2]. Alumina oxide is used to produce supported $CrO_x$ and Pt–Sn. The high acidity of the alumina is the main disadvantage of this support, which leads to side reactions. $SiO_2$, $TiO_2$, and $ZrO_2$ were studied as supports for dehydrogenation catalysts. Chromium oxide deposited on the surface of $ZrO_2$ was the most active in dehydrogenation reactions among the chromium-containing systems due to stabilization of chromium in the active highly dispersed states [3]. The method of co-precipitation is widely used to produce chromia–zirconia catalysts. Nevertheless, the influence of the synthesis conditions and the Cr/Zr ratio on the phase composition and the catalytic activity of such systems in the dehydrogenation of alkanes have been poorly studied. Thus, the present work is devoted to study of the influence of synthesis conditions and the Cr/Zr molar ratio of mixed Cr–Zr oxides on the physical-chemical and catalytic properties.

Two series of chromia–zirconia catalysts with different Cr/Zr molar ratio were prepared by co-precipitation method. The structure and chemical properties of mixed oxides were studied by low-temperature $N_2$ adsorption, XRD, DRS and TPR methods. The catalytic activity was tested in propane dehydrogenation.

The results of low-temperature $N_2$ adsorption indicate mesoporous structure of all synthesized catalysts. A series without ageing is characterized by changing of the specific surface area as chromium content increases. The specific surface area values for these systems vary from 24 ($ZrO_2$) to 107 $m^2/g$ ($Cr_{10}Zr_{90}O_x$). Further increase of the chromium content to 20 %mol. leads to a reduction of the specific surface area (77 $m^2/g$ for $Cr_{20}Zr_{80}O_x$). The values of the specific surface for aged samples vary in the range from 38 to 62 $m^2/g$, and for $ZrO_2$ (c) this value is 5 $m^2/g$.

According to the XRD results, a mixture of monoclinic and tetragonal phases of $ZrO_2$ observed for $ZrO_2$ support. An increase of the chromium content in the catalyst leads to stabilization of $ZrO_2$ mainly in the tetragonal modification. The tetragonal phase of $ZrO_2$ in mixed oxides obtained with ageing prevail even at low chromium contents, while the $Cr_1Zr_{99}O_x$-$Cr_5Zr_{90}O_x$ samples without ageing are mainly represented by the monoclinic $ZrO_2$ phase.

The results of TPR-$H_2$ show two broad peaks of hydrogen consumption with temperature maximums at 351-383 and 488-535 °C for all catalysts. These peaks can be attributed to the reduction of $Cr^{+5/+6}$ into $Cr^{3+}$.

Catalytic tests for mixed oxide catalysts in the propane dehydrogenation showed that the catalysts prepared without ageing were more active. This may be due to the higher content of $Cr^{5+/6+}$, which can be reduced.

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# The reaction path between Magnesium Oxide nano-and subnano clusters and a chlorinated aliphatic compound with the Density Functional Theory: the edge effect

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Aerogel of magnesium oxide is a material with potential application in environmental remediation in soils and waters, given its attributed properties in adsorption and dehalogenating of halo-alkane compounds [1-3]. The environmental application is an intriguing and prospective avenue for environmental remediation, and requires thorough studies on the reactivity of aerogels in this context with haloalkane and also with haloaryl compounds as these ones are frequently found in environmental samples at ecotoxicological disaster sites, encompassing crude oil spills, soil-contamination by petroleum products and other affected aquatic and terrestrial environments due to industrial and logistic pollution. The problem of petroleum contamination in the environment with particular emphasis on oil spills has been known for decades; however, with the incidents of the Deep water Horizon disaster and the Prestige Oil spill, new emphasis on remediation and degradation of oil-residues has arisen.

In this context, a potentially ideal candidate for oil remediation is magnesium oxide, MgO, in the form of nano-and subnano clusters. Therefore, this dispersed form has been analyzed here towards the reactive properties with haloalkanes using quantum chemical methods. The structures of the MgO clusters have been generated with symmetry-rules to study adsorption modes and the reaction paths of MgO clusters (with 2, 3, and 4 layers, that is, up to 64 atoms) with chloroethane as a representation structure for the haloalkanes. Calculations with the Gaussian and ORCA suite of programs were conducted with a conventional def2-SVP all-electron basis set and a recently developed by Alberto Otero-de-la-Roza and Gino A. DiLabio (2017) effective core potential with electron basis set for the BLYP and B3LYP density functionals. ChemCraft program was applied for analysis of results obtained with the Gaussian and ORCA suite of programs. This modeling was done in order to verify the hypothesis proposed by Mishakov et al. (2001) [2] who reported the likelihood of a spontaneous conversion of chloroethane to ethene and hydrochloric acid in one reaction, catalyzed by MgO nanoparticles, through three different paths.

Two types of point structural defects, i.e., neutral as well as charged, namely, [$Mg^{2+}$•MgO] and [$O^{2-}$•MgO], were modeled for the chemically pure system. In addition, small clusters were doped by Cr, Fe or Na atoms to investigate the effect of the induced local structural disturbance by the controlled impurity. It is worthwhile to note that the MgO, CrO, FeO bulk phases are assigned to the NaCl structural type. The structures with the void defects were studied with the water molecule as a co-adsorbate. The adsorption energies for different sites were obtained for the pristine surfaces coinciding with MgO (100) as well as for the edge sites of the nano-and subnano clusters. Surface regeneration in case of the void defects in presence of water molecules was observed. A reaction path of EtCl dissociation for the ridge site was determined and, thus, the catalytic reaction was established at the chosen quantum chemical theory level.

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# Conversion of inulin to mannitol with magnetically recoverable catalysts

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Polyols are important materials which are widely used in various fields. Mannitol, $C_6H_{14}O_6$, is employed in pharmaceutical, chemical, and food industry as well as in biotechnology. It is used to treat brains diseases, as a food supplement (E421) and a sweetener in diabetic foods, in the production of resins, linseed oil, coatings, surfactants, explosives, and cosmetics. These numerous applications determine the high demand for mannitol.

The polysaccharide hydrolytic hydrogenation can be carried out as a one-pot procedure in the presence of heterogeneous catalysts containing various precious metals. The Ru-based catalysts are considered the most active.

Magnetically separable catalysts received considerable attention due to easy magnetic separation from reaction mixtures, facilitating the catalyst repeated use and allowing one to save energy and materials, thus decreasing the target product costs.

In our preceding work, we developed Ru-containing magnetically separable catalyst based on magnetic silica ($Fe_3O_4$-$SiO_2$), where magnetite and Ru nanoparticles are formed in the silica pores. This catalyst allowed 100 % of cellulose conversion and the formation of ethylene glycol and propylene glycol as target molecules. Here, we explore a similar Ru-containing magnetically separable catalyst in the inulin hydrolytic hydrogenation to mannitol. We demonstrate the catalyst high activity and stability in repeated uses with the 100 % inulin conversion and the 44.3 % selectivity to mannitol.

The experiments were performed in a steel reactor (50 mL, Parr Instruments, USA) equipped with a controller PARR4843. Inulin (0.3 g), a catalyst (0.07 g), and 30 mL of distilled water were loaded into the reactor. Then the reactor was purged with hydrogen three times under 60 bar pressure. The mixture was heated and stirred (~100 rpm) to prevent the formation of local hot spots and the catalyst surface was saturated with hydrogen. After reaching the operating temperature the stirrer speed was increased to 600 rpm. This moment was chosen as the reaction starting time. At the end of the experiment the catalyst was separated by a neodymium magnet. The non-hydrolyzed polysaccharide, if any, was separated by filtration. The content of the main products was determined by liquid chromatography using UltiMate 3000 (Dionex, USA).

After the catalytic reaction, the liquid phase contained mannitol, sorbitol, glycerol, and propylene glycol along with other trace polyols, whose amounts depend on the experimental conditions. To achieve the highest possible selectivity and the complete inulin conversion as well as high activity, a number of reaction parameters such as temperature, reaction duration, hydrogen partial pressure, and the Ru/inulin ratio has been varied. To evaluate the catalyst stability, the catalyst was separated from the reaction medium using a neodymium magnet and used in the following experiments.

In the hydrolytic hydrogenation of inulin, the maximum selectivity to mannitol of 44.3 % was obtained at 150 °C, $P(H_2)$ 60 bar, 0.1167 mmol of Ru per 1 g of inulin for 45 min with the catalytic activity of 2.53 $h^{-1}$. Under these conditions, the inulin conversion reached 100 %. It is noteworthy that the selectivity reported here exceeds that of commercially available Ru/C. This and the excellent catalyst stability under hydrothermal conditions as well as easy magnetic separation make 5 % Ru-$Fe_3O_4$-$SiO_2$ the catalyst of choice for practical applications in biomass conversion.

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# The influence of the order of active component introduction on catalytic properties of Mo–Fe–O/$SiO_2$ catalysts in selective oxidation of 1, 2-propanediol

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The priority challenge of modern science is the opportunity to use the products of processing of renewable natural sources. For instance, propylene glycol can be produced via the processing of biomass, biodiesel and by-products of these processes [1]. In its turn, propylene glycol is an in-demand raw material that produces valuable organic compounds, such as methylglyoxal, hydroxyacetone, lactic acid, etc., during its catalytic oxidation.

Fe–Mo–O catalysts, due to industrial application in methanol oxidation to formaldehyde, are widely studied [2]. However, an interest in such systems grows steadily. In the literature, the studies of bulk Fe–Mo–O catalysts are mainly presented. In some cases supported catalysts posses the activity, which was close to the one of industrial catalysts [3]. Therefore, the aim of the present work is to synthesize the supported Mo–Fe–O/$SiO_2$ catalysts with different Mo/Fe ratio and to study the influence of the preparation method on the phase composition and catalytic properties of the obtained catalysts in propylene glycol oxidation to methylglyoxal.

The Mo–Fe–O/$SiO_2$ catalysts were synthesized by methods of sequential and joint incipient wetness impregnation. Silica (KSKG, LLC "Salavat Catalyst Plant", with surface area of 300 $m^2/g$) was used as a carrier. A series of Mo–Fe–O/$SiO_2$ catalysts was synthesized by the co-impregnation method with citrate solution containing both ammonium paramolybdate and ferric nitrate in corresponding concentrations. The Mo/Fe molar ratio varied from 0.5 to 3. The resulting samples were dried at 120 °C and calcined in air flow at 550 °C. For the series of $MoO_3/Fe_2O_3/SiO_2$ and $Fe_2O_3/MoO_3/SiO_2$ catalysts prepared by sequential impregnation by varying the order of introduction of the components, the Mo/Fe molar ratio was 3. The resulting samples were dried at 120 °C and calcined in air flow at 550 °C after each impregnation step.

The catalysts were characterized by XRD, UV-vis, Raman spectroscopy, low-temperature $N_2$ adsorption and TPR methods. The catalytic properties of the Mo–Fe–O/$SiO_2$ catalysts were studied in the gas-phase propylene glycol oxidation to methylglyoxal at the temperature 350°C (mixture composition: 3% $C_3H_6(OH)_2$, 3.7% $O_2$, 62% $N_2$, 30% $H_2O$). The major reaction products were methylglyoxal, formaldehyde, and hydroxyacetone.

According to catalytic test data, propylene glycol conversion of 18% and selectivity towards methylglyoxal of 41% were observed over the Mo–Fe–O/$SiO_2$ catalyst with the lowest content of iron oxide (Mo/Fe=3) prepared by co-impregnation method. For catalysts prepared by the sequential impregnation method (Mo/Fe=3), the order of introduction of the components on the support surface is shown to play an important role. Thus, for the $MoO_3/Fe_2O_3/SiO_2$ catalyst (the support is firstly impregnated with an iron nitrate solution and then with ammonium heptamolybdate solution), methylglyoxal selectivity of about 63% with a propylene glycol conversion of 15% are obtained. In the reverse order of the introduction of components, a decrease in total activity of $Fe_2O_3/MoO_3/SiO_2$ catalyst was observed along with the predominance of selectivity for hydroxyacetone, which indicates a change in the mechanism of the propylene glycol oxidation reaction. The report will present and discuss the scheme of transformations taking place on the surface of Fe–Mo–O/$SiO_2$ catalysts.

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# The role of metallic component (Pt, Pd) in Pt(Pd)/$WO_3$/$ZrO_2$ catalysts for isomerization of n-heptane

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Currently, environmental safety of motor fuels is given special attention. The quality of gasoline produced in Russia is regulated by the Technical Regulations of the Customs Union [1]. According to the requirements [1] in commercial gasolines, the content of aromatic hydrocarbons is strictly limited (for gasoline of ecological class 5 there should be no more than 35 % vol.). The present work is aimed at studying catalysts for a new process of straight-run gasoline fraction 70-105 °C, containing mainly heptanes, in the direction of isomerization. The introduction of this technology into the oil refining industry will make it possible to produce a high-octane non-aromatic hydrocarbon component of gasoline, which will facilitate the production of modern ecological gasolines of class 5.

The catalysts for the isomerization of n-heptane (model feed) investigated in this work are bifunctional. The acid function in the catalysts is performed by tungstated zirconia $WO_3/ZrO_2$, the platinum group metal (platinum, palladium) corresponds to the hydrodehydiration function. The acid component of the catalysts was prepared according to the procedure given in [2, 3]. The most active and selective $WO_3/ZrO_2$ sample is containing 25 wt. % $WO_3$ and calcined at 950 °C [2, 3]. Platinum and palladium in $WO_3/ZrO_2$ catalysts were introduced from $H_2PtCl_6$ and $H_2PdCl_4$ solutions, respectively.

The role of the metal component (Pt, Pd) in $WO_3/ZrO_2$ catalysts was studied. Studies have been carried out on the effect of the concentration of Pt, Pd in catalysts in the range 0.05-2.0 wt. % on acidic and catalytic properties in the isomerization reaction of n-heptane. It is shown that in order to achieve a comparable yield, the sum of heptane isomers is 71-74 wt. and di- and trimethyl-substituted high-octane isomers of heptane (DTMS) of about 29 wt. %, the content of platinum in the catalysts should be provided at a level of 1.0-1.5 wt. %, and in the case of palladium catalysts, the active metal content can be reduced by 10-15 times (0.1 wt. %).

The charge state of platinum and palladium in tungstated zirconia catalysts is studied depending on the conditions of thermal activation. It was shown that in calcined catalysts there are platinum and palladium atoms in a charged and metallic state. It was found that the presence of charged Pt and Pd atoms in catalysts promotes an increase in the catalytic activity of the samples in the isomerization of n-heptane. Charged forms of platinum and palladium are formed during the calcination of Pt(Pd)/$WO_3$/$ZrO_2$ catalysts in the air flow.

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# Theoretical and experimental study of 2-methylimidazole formation

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The interaction of mono- and dicarbonyl compounds with ammonia and amines leads to the formation of a valuable class of aromatic compounds, namely, imidazoles. These a liquid-phase processes underlie the synthesis of most nitrogen-containing heterocycles. These heterocycles are widely used in all fields of science and life, including the development of a new generation of drugs and production of polymers. These compounds are also a part of insecticides and various dyes.

The methods of synthesis of imidazoles are mainly described in patent literature. In this paper, we are focused on the synthesis of imidazoles by the Debus-Radziszewski method [1, 2], i.e. the interaction of α-dicarbonyl compounds with ammonia and aldehydes, in particular, the reaction of glyoxal with ammonia and acetaldehyde to form 2-methylimidazole [3, 4]. The accurate data on the mechanism as well as thermodynamic and kinetic regularities of this process have not been found in the literature. At present, the reaction of acetaldehyde with ammonia [5] and the reaction of glyoxal with ammonia [6] in the aqueous medium are studied separately. The products of such interactions are identified. In the case of acetaldehyde–ammonia interaction, 2,4,6-trimethyl-1,3,5-hexahydrotriazine is a reaction product, while in the case of glyoxal–ammonia system, a series of equivalent C–N oligomers containing imidazole rings are formed. The mechanisms of these processes were suggested, their kinetics was studied by various methods of physical-chemical analysis.

Thus, the present work is aimed to determine the mechanism, kinetic and thermodynamic parameters of the 2-methylimidazole formation process by quantum chemical calculations combined with experimental data obtained using NMR spectroscopy.

In the present work, the schemes of the interactions between intermediates of acetaldehyde–ammonia and glyoxal–ammonia interactions resulting in the formation of 2-methylimidazole by the Debus method are proposed. A complete analysis of the potential energy surface (PES) of these mechanisms was carried out. A regular series of intermediate compounds participating in the most favorable pathway of the aromatic product formation are determined.

The calculations were carried out using the Gaussian'09 software package at the B3LYP/6-311G (d,p) level of the theory. The total free energy of the system in solution, taking into account solvation (PCM method), was used to construct the potential energy surfaces (PES). The solvation energy includes electrostatic and non-electrostatic contributions.

The kinetic data of the formation of 2-methylimidazole in the reaction of glyoxal and 2,4,6-trimethyl-1,3,5-hexahydrotriazine (adduct of acetaldehyde and ammonia) in water solution as well as data on the structure of possible intermediates were obtained by the method of NMR spectroscopy.

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# SECTION 4

## INDUSTRIAL IMPLEMENTATION OF CATALYTIC PROCESSES

# Некоторые особенности промышленного катализа процесса окисления циклогексана

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Современное производство капролактама является многотоннажным (6.880 млн тонн по данным 2016 г [1]) и многостадийным процессом, который базируется на промежуточном образовании циклогексанона из циклогексана или фенола, с его дальнейшим оксимированием и перегруппировкой получаемого оксима в капролактам (Asahi Process).

Доля использования бензольного сырья в производстве капролактама составляет около 78 %, фенольного – 19 %, остальное приходится на толуол. В настоящее время около 95 % мирового производства капролактама базируется на классической технологии Asahi Process, а менее 5 % - на технологии прямого синтеза циклогексаноноксима из циклогексана фотонитрозированием (Toray Process) и на технологии прямого синтеза из толуола последовательными реакциями окисления, восстановления и нитрозирования (SNIA – Viscosa Process). Есть сведения о совместной разработке новой технологии компаниями DuPont и Shell, которая полностью отличается от традиционного способа, так как основана на использовании доступного и относительно дешевого вида сырья, включающего бутадиен, CO, $NH_3$ и $H_2$. Altam process находится на завершающей стадии разработки и, по мнению специалистов, может стать доминирующим мировым технологическим процессом получения капролактама.

Несмотря на отлаженную технологию и длительный опыт эксплуатации в промышленности, эффективность превращения циклогексана в циклогексанон (промежуточный продукт производства капролактама) остается низкой. Стадия окисления циклогексана характеризуется наибольшими энергозатратами из-за низкой конверсии – 4 ÷ 5 % и необходимости рецикла циклогексана, а также образованием большого количества побочных продуктов. Селективность промышленного процесса находится на уровне 80 ± 3 %.

В работе приводятся сведения о крупных мировых производителях капролактама, сравнительные показатели существующих технологий, результаты усовершенствования отдельных стадий, преимущественно по стадиям окисления циклогексана и выделения циклогексанона из оксидата. Более подробно рассказывается о существующих проблемах и о потенциале улучшения производственных показателей на примере конкретного производства капролактама на производственной площадке КАО «Азот».

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# Макропористые носители и катализаторы на их основе

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В докладе представлены материалы по использованию макропористых носителей (размер пор от 0,5 до 5,0 мм.) для приготовления катализатора снижения вязкости высокосернистых и вязких нефтей Ашальчинского месторождения РТ и селективного гидрирования ацетилена в ЭЭФ ПАО «Нижнекамскнефтехим».

Показано, что в зависимости от условий проведения процесса (наличие или отсутствие водорода) протекает гидрооблагораживание с удалением до 25 % серы. При этом вязкость нефти необратимо снижается с 3000 сСт до менее 100 сСт за проход, за счет изменения группового состава. Увеличивается количество масляных фракций в результате снижения содержания смол. Количество асфальтенов не меняется.

Приготовление катализаторов селективного гидрирования ацетилена в ЭЭФ с использованием макропористых носителей позволяет увеличить селективность (по этилену) с 76 (лучший импортный образец) до 92 % при снижении активности с 31 до 28 %.

Использование макропористых носителей позволяет создавать эффективные катализаторы гидропроцессов в нефтепереработке и нефтехимии.

# Technological aspects of arctic fuels obtaining from associated petroleum gas

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Because of intensive development of the Arctic significantly growing requirement in arctic diesel fuel, that currently can be obtained only from oil stock. Arctic diesel fuel can be obtained by alternative way from associated petroleum gas (APG) by GTL(gas-to-liquids) technology in areas of oil production [1]. This technology will allow us to utilize APG, produce qualitative fuel that exceeds analogous oil fuel by ecologic and exploitation characteristics, and decreases deficit of this production type in Russian Federation.

Researches, performed in "Nanotechnologies and modern materials " institute SRSPU(NPI), showed principal opportunity of creating technology that allow to obtain arctic fuel from natural gases. Particularly, using of polyfunctional catalyst enable to synthesize diesel fraction with high amount of branched alkanes, which provide required low-temperature properties [2].

In current report showed results, which were obtained during the development of innovative technology of producing arctic diesel fuel from APG. Full-cicle pilot complex of conversion natural and associated petroleum gases into synthetic hydrocarbons has been created at SRSPU(NPI) for realization of this project. Moreover, the first in Russian Federation pilot-industrial installation of producing synthetic hydrocarbons from natural gases has been created. (PCF "Sverdlov Plant", Dzerzhinsk).

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