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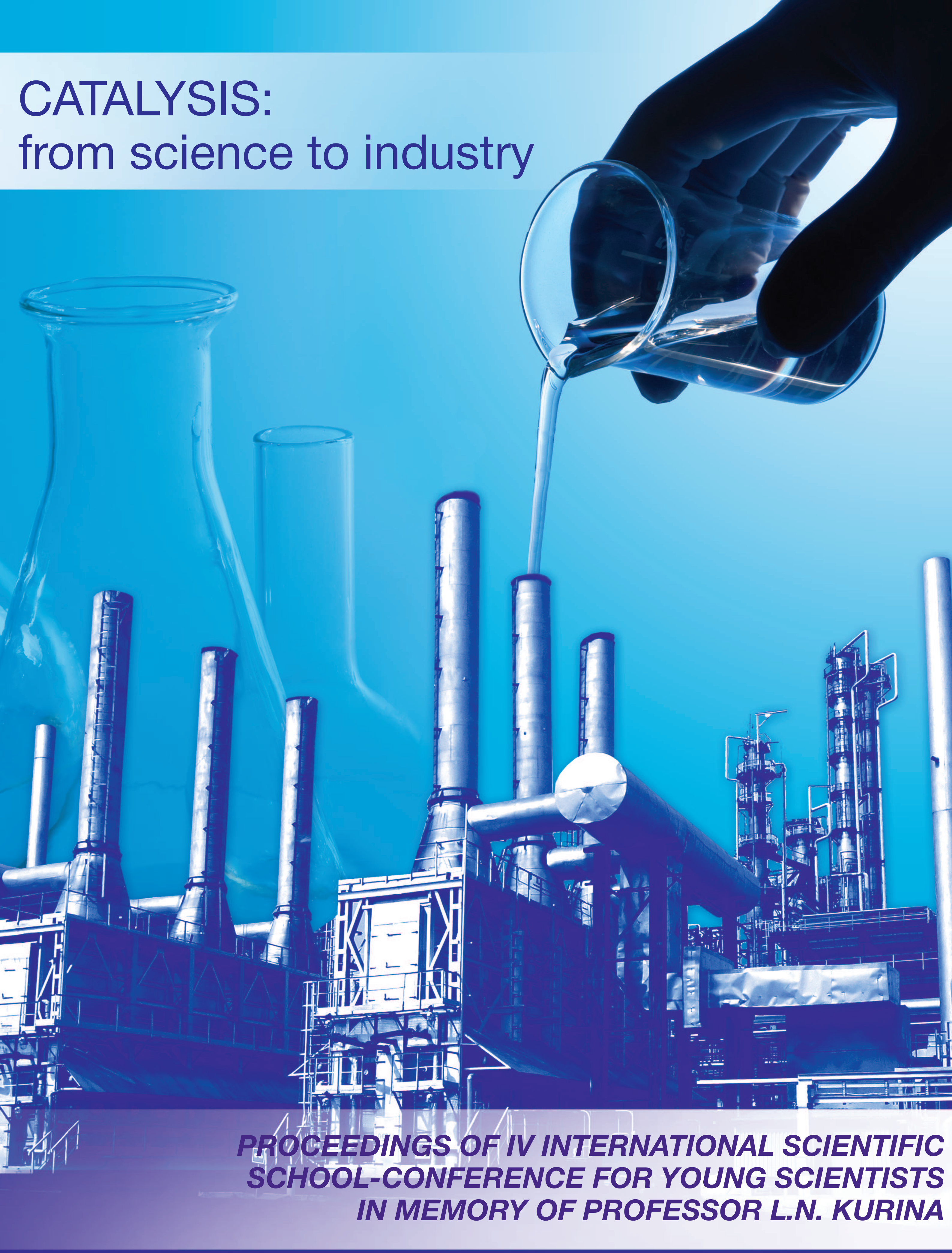
from science to industry



PROCEEDINGS OF IV INTERNATIONAL SCIENTIFIC SCHOOL-CONFERENCE FOR YOUNG SCIENTISTS IN MEMORY OF PROFESSOR L.N. KURINA

October 23-27, 2016
TOMSK

THE MINISTRY OF EDUCATION AND SCIENCE OF THE RUSSIAN FEDERATION
NATIONAL RESEARCH TOMSK STATE UNIVERSITY

CATALYSIS: FROM SCIENCE TO INDUSTRY

Proceedings of
IV International scientific school-conference for young scientists
in memory of Professor L.N. Kurina

October 23-27, 2016

Tomsk 2016

UDC 544.47/544.72+661.7
LBC 24.54
P75

P75 **Catalysis: from science to industry:** Proceedings of IV International scientific school-conference for young scientists in memory of Professor L.N. Kurina “Catalysis: from science to industry” / Tomsk State University. – Tomsk: “Ivan Fedorov” publishing, 2016. 136 p.

ISBN 978-5-91701-119-6

The collection is devoted to important and perspective directions of modern catalysis: fundamentals of catalyst preparation and catalytic processes, promising catalytic processes and industrial implementation of catalytic processes.

This event carries out with support of the Russian Foundation for Basic Research Grant 16-33-10424-mol_g.

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ИНЖИНИРИНГОВЫЙ ХИМИКО-ТЕХНОЛОГИЧЕСКИЙ ЦЕНТР

Эффективные решения для вашего бизнеса:
от проведения НИР/НИОКР до приемочных испытаний
технологии и малотоннажного производства продукта

ПОЛНЫЙ КОМПЛЕКС ИНЖИНИРИНГОВЫХ УСЛУГ ОТ ИДЕИ ДО ПРОМЫШЛЕННОГО ВНЕДРЕНИЯ

Порядка 80 завершенных и действующих проектов. Ведется испытание более 100 образцов продукции,
6 технологий передано в производство.

БОЛЕЕ 200 РАЗРАБОТОК

Партнерский доступ к научной базе, оборудованию и программному обеспечению ведущих вузов, национальных исследовательских университетов и научно-исследовательских институтов по всей России.

ПРОФЕССИОНАЛЬНАЯ КОМАНДА

Более 30 высококлассных специалистов в области разработки и внедрения наукоемких химических и биологических технологий. Это инженеры, технологи, ученые, маркетологи с опытом работы на ведущих химических предприятиях и в лучших вузах и НИИ России.

ДОСТУП К ЭКСПЕРИМЕНТАЛЬНЫМ И ОПЫТНО-ПРОИЗВОДСТВЕННЫМ ПЛОЩАДКАМ

с современным оборудованием наших партнеров в Томске, Новосибирске, Кемерово, Казани, Уфе, к уникальным программным продуктам, свежим разработкам и исследованиям.

МЫ НЕ ТРАТИМ ВАШИ ВРЕМЯ И ДЕНЬГИ ВПУСТУЮ

Оптимизация и настройка технологического процесса делается под конкретные задачи с учетом анализа рынка. Мы собираем оборудование, технологии, привлекаем специалистов отдельно под каждый заказ. В проекте задействованы лишь те инструменты, которые реально необходимы.

PLENARY
LECTURES

Modern trends in studies of low-temperature CO oxidation

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The low-temperature oxidation (LTO) is a rapidly developing field of heterogeneous catalysis. Theoretical basis is related with the catalysts capability to realize effective oxidation with high reaction rates and low activation energies. Thus, LTO is a powerful tool for studying the most effective ways of catalysis. Usually, the capability of catalysts in LTO is tested by reaction of carbon monoxide (CO) oxidation. This reagent is a most appropriate chemical probe testing the active centers of catalysts due to its small size, high adsorption and reaction probabilities. To date, it has become generally accepted the statements as follows: the decrease of CO adsorption enthalpy, increase of oxygen mobility and the separation of adsorption sites for CO and O_2. The most effective solution of these requirements can be connected with application of composite catalysts like metal-oxide systems.

In this work the general approaches in realization of effective oxidation are considered on the M-ceria based systems (M- elements of platinum group metals (PMG) or Ib group) [1-6]. Experiments show that addition of metal to ceria results in incorporation of metal to ceria lattice with dramatic change of the support properties, one of which the main features are the strong increase of oxygen vacancies concentrations and enhancement of oxygen mobility. In this relation one of the main modern trends in investigation of ceria based catalysts is a consideration of support as important part of active components in catalysts. The formation of solid solutions in metal-oxide systems provides high oxygen mobility that is necessary step to improve catalytic activity. Also, the formation of special surface structures is considered as a most important step in realization of catalytic cycle. The comparison of metallic and ionic species of active components and their role in CO oxidation will be discussed in this presentation.

Practical application of CO oxidation is very important in many fields of science and industry. The most perspective directions will be considered in this presentation, namely: the development of catalysts providing high activity in CO oxidation at low temperatures with preservation of their thermal stability and the capability of catalysts to oxidize CO in wet ambient.

This work was supported by RFBR Grant 14-03-01088.

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Some considerations on the (un)predictability of science

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Predictability in science advances and their transfer to industrial application has been a constant concern for decision makers whether they are scientific researchers, industrialists or politicians. Research history has shown however that many forecasted successes never became actual industrial applications and many unforeseen developments became huge successes for industry and society.

In the field of catalysis some hot topics are now being tackled and seem promising for future up scaling such as predictive catalysis (theory), nanostructured materials, single-site catalysis, single-atom catalysis, gold catalysis, advanced operando visualization of catalysts, VOC abatement, carbon dioxide capture, hydrogen production, biofuels, biomimetics,…

Some of the above mentioned subjects will be critically analyzed.

Ethanol steam reforming on non noble metal catalysts (Ni, Co)

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The increasing worldwide demand of energy and the environmental impact of the massive use of fossil fuels have boosted the interest of hydrogen as an alternative, clean energy vector. But on Earth hydrogen exists only combined in other compounds, and, being the lightest of the gases, its volumetric energy density is very low and it is difficult to transport, both strong handicaps for mobile uses. Thus, for reducing CO_2 emissions, renewable resources should be used to produce it and, for mobile applications, preferably liquids. Ethanol is advantageous over other conventional substrates because it is readily available, easy to obtain from biomass and to transport, CO_2-neutral and safe to handle.

Though noble metal-based catalysts are stable and very active for ethanol steam reforming; (ESR), they are expensive and need high reaction temperatures to be active. Nickel- and cobalt-based catalysts are inexpensive, but under reaction conditions they suffer from sintering and deactivation by carbon deposition [1]. The latter can be prevented by supports with redox properties, based on CeO_2, due to its oxygen storage capacity and high oxygen mobility. Besides, this type of catalytic systems is also active for preferential oxidation of CO (CO-PROX) [2]. The key for implementing their use is to improve their catalytic activity and stability.

With this objective, the catalytic behavior of nanostructured catalysts based on combinations of oxides of Ce, Ni and Co for ESR has been studied at 350-500°C and atmospheric pressure. Catalysts with different M/Ce (M = Ni, Co) ratios were prepared by coprecipitation within reverse microemulsions (RME) [3], method that allows to obtain nanostructured systems with a high structural morphologic and chemical homogeneity. In addition, some similar catalysts were prepared by conventional impregnation, for comparative purposes. They were characterized by S_{BET}, XRD and TPO and tested for ESR in a fixed bed, flow reactor. As prepared, the catalysts were basically formed by combination of the cubic phases: CeO_2, NiO and Co_3O_4, but upon reduction both Ni and Co were incorporated into the CeO_2 network.

The catalytic behavior of the H_2-reduced fresh catalysts depended strongly on the nature and content of the metal (Ni catalysts were more active than their Co homologues) and the preparation method. The most efficient catalyst was the monometallic with the highest Ni amount prepared via reverse microemulsions, which gave almost complete ethanol at 500 ºC with 50% hydrogen selectivity, and was stable for at least 22 h on stream. All the other catalysts deactivated due to carbon deposits generated through acetone and ethylene formation, as proven by TPO of used catalysts. However, initial conversion values can be recovered (for Ni catalysts), or even higher values can be reached (for Co-containing catalysts), by high temperature oxidative reactivation treatment. The important improvement of performance (both in activity and stability) and the change of product distribution observed after oxidative regeneration for Co-containing catalysts prepared by RME point to a restructuration of the active centers during the reaction-reactivation cycle.

This work was supported by MINECO (projects CTQ2012-32928 and CTQ2015-71823-R). The valuable collaboration of A. Martinez-Arias, C.L. Bolivar, I. Carbajal, M.V. Vidal Mejía and N. Pinton on this subject is warmly acknowledged.

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Anion-modified Metal Oxides: «New Possibilities» of «Old Catalysts» for the Production of Motor Fuels

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Production of motor fuels is an important direction of development of the world economy, including Russia. The efficiency of any oil refineries is determined by quality and environmental safety of motor fuels. Present-day requirements for ecological safety of motor fuels include the severe restrictions of aromatic hydrocarbons and sulfur compounds content in commercial gasoline and diesel fuel.

The implementation of environmental requirements is based on the development of processes for synthetic motor fuels production from C_2-C_4 alkenes by catalytic oligomerization, alkylation of isobutane, etc. It should be noted that the raw materials (ethylene, propylene and butylene fractions) for these processes may be obtained not only by pyrolysis and cracking of crude oil but also by the Fischer-Tropsch process and oxidative pyrolysis of natural gas or biomass. Researchers pay special attention to the industrial implementation of hydrotreating processes of carbonaceous raw materials as another way to produce environmentally friendly motor fuels. The most important among them are hydroisomerization of benzene-containing gasoline fractions for low benzene content gasoline production and one step hydrocracking of vegetable oils for diesel fuels production.

Industrial processes of propylene or butenes oligomerization and isobutane alkylation are carried out on special acidic catalysts such as "solid phosphoric acid", sulfonic resins, liquid acids (H_2SO_4, HF). "Solid phosphoric acid" has a short life span (6-12 months) and can't be regenerated and reused because of loss of mechanical properties by cementation. The usage of sulfonic resins is limited by their low temperature stability (up to 130 °C). Liquid acids (H_2SO_4, HF) as alkylation catalysts cause the corrosion equipment and environmental pollutions. The principal disadvantage of liquid acids is a necessity to separate products mixture and liquid catalyst. Vegetable oil hydrotreating for diesel fuels production is a two-step industrial process with catalysts of different nature. The first stage is hydrocracking on sulphide catalysts Co(Ni)-Mo(W)-S. The second stage is alkane hydroisomerization on bifunctional catalyst that is needed to provide low temperature properties of diesel fuel.

Meanwhile, the heterogeneous acidic and polyfunctional systems based on anion-modified metal oxides can be used as catalysts for ethylene and C_3-C_4 alkene oligomerization, for alkylation of isobutane with butenes, for one step diesel fuel production from vegetable oils and for hydroisomerization of benzene-containing gasoline fractions. Besides the activity and selectivity advantages of these catalysts include simplicity of industrial production and low cost. Thermal stability of the catalysts provides the possibility of multiple oxidative regeneration. As a part of this work the possibilities of preparation and testing of catalysts based on borate-containing and sulfate-containing alumina and zirconia are examined. The chemical composition of these catalysts and consequently average acidity of the borate-containing alumina provide the double bond isomerization of alkenes, alcohols dehydration, propylene and butene oligomerization. Also sulfated zirconia is well known to have high activity in low temperature alkene isomerization and isobutane alkylation. One of the practical reasons to use these catalysts is our wide experience in industrial preparation of highly porous alumina and zirconia and catalysts based on these systems.

Ni-based catalysts for methane dry reforming: effects of Ni active sites and support composition

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Nowadays the use of CO_2 and CH_4 as chemical feedstock may contribute to reduce effectively such greenhouse gases in the atmosphere. Dry Reforming of Methane (DRM) has received considerable attention as an attractive route to produce syngas, CO + H_2, which main application is electricity generation and as intermediate in producing synthetic petroleum via Fischer–Tropsch synthesis. 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 [1]. 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 Pt, Au, Pd may reduce poisoning and deactivation.

My research group has recently found for a trimetallic catalyst, $NiAuPt/Al_2O_3$, improved catalytic activity and stability to carbon poisoning with respect to monometallic Ni and bimetallic Ni-Au and Ni-Pt systems [2]. This promoting effect was attributed to the formation of high active Ni-Au-Pt nanoparticles, synergistically interacting. The support composition, such as the use of CeO_2-Al_2O_3 or MgO-Al_2O_3, also plays an important role on Ni activity and stability.

In present work, details on structural and surface investigations, by EXAFS and CO-FT-IR analyses carried out on $NiAuPt/Al_2O_3$ catalysts will be discussed.

The authors acknowledge the financial support provided by Italy, EFOR-CNR Project (Energies by Renewable sources) and by European Community, COST Action CM 1104. Dr. Francesco Giordano from ISMN-CNR is gratefully acknowledged for XRD measurements.

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Structural aspects of formation of catalytically active nanoparticles on surface of various supports

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Fine metal and oxide particles supported by various oxides are an important class of catalytic systems. The surface of oxide support can strongly affect the degree of dispersion, structure and catalytic properties of supported nanoparticles. Structural characterization is known to play key role in understanding of catalyst structure-activity relationships. The most interest is in the structure of catalytically active nanoparticles. However, traditional routine XRD methods are usually ineffective for this study. The contribution to XRD pattern originating from small fraction of active component is insignificant in most cases. Moreover, diffraction patterns of highly dispersed materials are characterized by strong background and broadened peaks. Radial distribution function (RDF) of electronic density or atomic pair distribution function (PDF) method is effective for studying the local structure (short range atomic arrangement) of nanoparticles. This method is based on the Fourier relationship between intensity of coherent X-ray scattering and RDF of electronic density [1, 2]. Using this technique, one can directly define interatomic distances and coordination numbers of atomic arrangement. To determine features of the local structure of supported nanoparticles as against well crystallized analogues a comparison of the experimental RDF and the model one constructed on the basis of known structural data is used [3].

In this work we report some examples of the RDF analysis application: 1) to determine the structure of highly dispersed active component in supported catalysts 2) to elucidate structural aspects of interaction between the support and active component.

The Au(Pt)/γ-Al_2O_3 catalysts with different metal content were considered. RDF data strongly suggested an epitaxial interaction between supported metal Au and Pt particles and the surface of support. Such interaction may be a reason for high thermal stability of supported metallic nanoparticles.

The Cu/ZrO_2 catalysts with tetragonal (t) and monoclinic (m) zirconia were considered. It was shown that Cu/t-ZrO_2 catalysts contained undetectable by usual XRD analysis highly dispersed copper species. RDF analysis revealed that copper (II) oxide chain clusters and chain network were the main copper species, while particles with CuO bulk structure were not formed significantly. Moreover, the obtained data were in agreement with the incorporation of some copper ions into zirconia lattice. RDF data also suggested interaction of active component with zirconia surface in Cu/m-ZrO_2 catalysts, which efficiently stabilized small CuO particles. The model of epitaxial growth of CuO particles on certain planes of m-ZrO_2 was proposed.

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Scanning electron microscopy study of platinum catalysts etching

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To study the physical and chemical characteristics of solid materials a variety of physical methods of research are used. The most widely used method for research and measuring physical properties of various materials is scanning electron microscopy (SEM). This method allows obtaining a number of different properties of the micro- and nanoobjects by scanning the electron probe. Due to the significant progress in the development of electron microscopy settings of the electronic probe are widely varied in the current scanning microscopes. It makes this method extremely flexible not only for research but also for the characterization of materials. SEM can be easily integrated into a single tool with such applications as X-ray microanalysis (PMA), electron backscatter diffraction (EBSD) and several others, which greatly expands the possibilities for the analysis and characterization of micro - and nanomaterials. Using of these applications allows carrying out a comprehensive study of various material characteristics, such as morphology, chemical composition and structure. Application SEM allows imaging material surface in the range of magnification from 10 to 1 000 000x with resolution, reaching less than 1 nm. The current trend in the development of SEM is associated with application of the electron probe with low energy electrons. Modern microscopes allow to obtain microscopic images of objects in a wide range of magnifications with high resolution when the probe electron energy is varied from 30 keV to 100 eV. Reducing the energy of the electrons in this range allows you to change the depth of penetration of the electrons in the volume of material from a few microns to a few nanometers. As a result, it is possible to vary the depth of the analysis in such a range that allows analyzing the volume of the material and its surface. This mode is commonly used for studying catalysts, since the active component of catalyst is distributed not only on the catalyst surface, but also in its volume. The variation of the probe electron energy allows us to analyze the distribution of the active component in the volume of catalyst granule.

Ammonia oxidation with air on platinum catalyst gauzes is widely used in chemical industry for synthesis of nitric acid. It is well known that during this process the gauzes undergo deep structural rearrangement of surface layers (catalytic etching) leading to the platinum loss and catalytic activity decrease. To reveal the mechanism of the catalytic etching of platinum catalyst gauzes during the NH_3 oxidation, we studied in detail the surface microstructure of the front and back sides of platinum catalyst gauzes used in ammonia oxidation. The platinum catalyst gauzes used in the study were made from a polycrystalline wire with $d \approx 82$ μm with the chemical composition (in wt.%) 81% Pt, 15% Pd, 3.5% Rh and 0.5% Ru. The surface microstructure was studied using a scanning electron microscope (SEM) JSM-6460 LV (Jeol) and SU8230 (Hitachi). This result seems to suggest that the etching develops in the course of gradual growth and transformation of the grains into crystalline agglomerates during the growth and merging of etching pits at the grain boundaries. Through pores with the size of 1-5 μm inside the agglomerates may be formed during merging of growing etching pits on the surface and in the bulk of the grains. The emergence and growth of the pits can be related to the reaction of ammonia molecules with oxygen atoms absorbed at the grain boundaries, dislocations and other surface defects. The reaction of gaseous NH_3 molecules with absorbed oxygen atoms O_{abs} with the formation of gaseous NO results in local overheating of the surface initiating the release of metal atoms to the surface. Intense release of metal atoms from pits at the grain boundaries forms extended voids between the grains. Metal atoms released from the defects quickly migrate over the grain surface and are gradually incorporated at the energetically most favorable sites. As a result, the grains are gradually reconstructed into faceted crystalline agglomerates with through pores formed due to the growth and merging of pits. When these processes go on for a long time, a rough corrosion layer including crystalline agglomerates with through pores separated by deep extended void is formed.

This work was supported by Russian Academy of Sciences and Federal Agency of Scientific Organizations (project 44.1.17).

KEYNOTE
LECTURES

Ultrafast optical spectroscopies reveal the mechanisms of photocatalysis

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Since the invention of pulsed lasers, time resolved spectroscopic methods observed tremendous developments. The research around the world in different fields from physics and chemistry to biology, medicine and material science, widely utilize ultrafast optical spectroscopies nowadays.

With pulse duration of 100 fs or less, it is possible to access most of the dynamics occurring in the excited electronic states: internal conversion, vibrational relaxation, intersystem crossing and many other processes leading to reactive pathways. The interplay between different electronic states often corresponding to different molecular geometries can be revealed and these studies can be profitable for the conception of new intelligent materials.

During the conception of novel materials, the efficiencies of functional processes (electron transfer, energy transfer, geometry changes) in most cases are related to their rate:

FAST = EFFICIENT,

since the losses of the population towards competitive side reactions and relaxation channels can reduce significantly the efficiency of desired processes and at worst can destroy the molecular systems.

Ultrafast spectroscopies are one of the best tools to reveal all relaxation pathways from excited states and to propose the solutions to block parasite reactions thus enhance desired functionalities.

In this report, I will present numerous applications of practical value we continue to develop exploiting photoinitiated electronic processes in molecular and supramolecular systems. Since molecular association affects the energies of electronic levels, chemical recognition is among the most natural applications exploiting the energy and electron transfer in these supramolecular compounds [1]. As well as chemical sensing when energy or electron transfer is present but also singlet oxygen generation can be obtained, fluorescence of rare earth ions can be exalted, etc.

A special attention I will draw on the first steps of some photoinitiated catalytical reactions we have studied. The first example concerns the Copper catalyst activation driven by photoinduced electron transfer [2] and the second deals with a supramolecular photocatalyst for the reduction of Au(III) to Au(I) [3]. Additionally, I will show some examples of electronic energy storage [4, 5, 6] and chemical energy storage [7] which could be used as energy reservoirs for low concentration applications.

I thank the ERA.Net Rus Plus program (project DONOS-311) for financial support.

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Chromia-alumina catalysts for fixed-bed dehydrogenation of light alkanes: from grams to kilograms

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The catalytic dehydrogenation of light alkanes into corresponding unsaturated hydrocarbons is an important industrial process for petrochemistry, chemistry, polymers, etc. The dehydrogenation of C_3-C_5 hydrocarbons in Russia is realized predominantly in fluid bed reactors with microspherical alumina-chromia catalysts. The processes with fixed bed or moving bed of the catalyst like Catofin, Oleflex, Star are used in Russian industry ever due to the absence of Russian-made catalysts. Thus, development of new catalysts for a fixed-bed dehydrogenation of light paraffins is an important challenge for Russian petrochemical and catalytic industry.

The creation of catalysts within the research lab is limited by lab equipment, while another reagents, productive facilities and conditions are used in the industrial manufacturing of the catalysts. The challenge to scale-up the catalyst preparation method from lab to industry was and is of importance for research groups developing the catalysts. The main idea of this topic is to show some examples of synthesis of alumina supports and chromia-alumina catalysts for dehydrogenation of paraffins from several grams to several kilograms taking into account the features of the feed used, reagents, conditions of preparation and treatments.

The first problem consists in the properties and purity of the feed which are used in industry to manufacture catalysts and which are different compared to those used in the lab (e.g., Sigma-Aldrich, Acros, etc.). Thus, there are some industrial precursors of Al_2O_3 which can be used (thermochemically activated aluminum trihydroxide, boehmite prepared by re-precipitation, etc.). All precursors of alumina are inhomogeneous in terms of phase composition and comprise boehmite, gibbsite and amorphous alumina. The ratio between these phases in the precursor depends on the production conditions and may differ from one lot to another. Particle sizes, wetness, loading of the main compound may also be differ which influences on the porosity, acid-base properties, strength of support granules and must be controlled in the lab prior to each synthesis. The type of precursor of active components and modifiers also should be chosen very carefully to maximize the loading of the active phase in the precursor and minimize the emissions of NO_x, HCl, Cl_2 and other compound which are aggressive to industrial equipment, human health and environment.

The conditions of mixing, dissolving, impregnation, drying and calcination significantly determine the homogeneity of the component states and distribution in catalysts granules. For instance, it was shown that the dissolution of alumina supports took place during the impregnation by aqueous solution of the concentrated chromic acid ($pH<0$). Fast impregnation or impregnation under vacuum may be used to minimize the time of contact of solution and support and prevent dissolution.

The conditions of drying and calcination are also different in the lab and industry. Thus, the stationary drying boxes and ovens are used in the lab, while belt, cylindrical and shaft driers and ovens with good mixing and treatment by air or inert gas flow are used in industry. This significantly increases the effectiveness of drying and calcination and provides high homogeneity of the product properties. On the other hand, the conditions of drying and calcination determine the porosity of the support or catalyst as well as distribution and state of components in the porous structure of support. Thus, the conditions of all operation in lab synthesis must be similar to those in industry.

The problem of standardization of measurements in the lab and industrial labs should be taken into account due to different applied equipment, methods, approaches, standards. Such properties of support and catalysts as size and shape of granules, strength, porosity (including macropores), volume weight, etc. is very important for industrial catalysts because they determine the competitiveness of the product.

This work was supported by the federal target program “Research and Development in the Priority Areas of the Science and Technology Complex of Russia for 2014–2020“ (contract no. 14.578.21.0028, RFMEFI57814X0028).

Methane transformation into syngas on ceria-containing catalysts

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Design of catalysts able to efficiently transform methane/natural gas/biogas into syngas in the intermediate temperature range without coking is an important task in the hydrogen energy field including internal reforming of fuels in solid oxide fuel cells and synfuels production. In this lecture results of the extensive international collaboration aimed at solving this problem are presented. The main point is that using ceria as a key component of nanocomposite catalysts comprised of complex mixed oxides with supported metal/metal alloys nanoparticles allows to achieve a high performance and coking stability in reactions of partial oxidation, steam and dry reforming of natural gas [1-6]. This is explained by operation of so called bifunctional mechanism of fuels transformation into syngas on this type of catalysts including activation of methane on metal sites, oxidants –on metal oxide sites generating reactive oxygen species rapidly migrating to metal-oxide interface transforming activated CH_x species into syngas. Hence, phase stability of complex oxide supports in reducing conditions, their high surface/near surface oxygen mobility and strong metal-support interaction/developed metal-oxide interface are key factors provided by presence of cerium in mixed oxide supports (mainly, with fluorite-like structure) ensuring high activity and performance stability in real operation conditions.

Next basic problems are considered [1-6]:

1) Effect of complex fluorite-like oxides (ceria-zirconia solid solutions, etc) preparation procedure (citrate route, Pechini route, synthesis in supercritical alcohols) and chemical composition on the phase composition, structural features and spatial uniformity of elements distribution between oxide nanodomains (by TEM with EDX), which were shown to be crucial parameters affecting oxygen mobility in these systems;
2) Effects of metals (Ni, Pt, Ru, Ni+Pt, Ni+Ru) interaction with supports on their local surface structure and reactivity (by XPS, FTIRS of adsorbed CO, TPR, TAP, etc);
3) Characterization of oxygen mobility and bonding strength in nanocomposite catalysts (especially, in steady-state conditions) by using oxygen isotope heteroexchange, SSITKA and pulse microcalorimetric methods;
4) Estimation of the rates of separate stages by unsteady-state kinetic methods (SSITKA, chemical transients, pulse methods including TAP);
5) Specificity of mechanism and kinetics of methane transformation into syngas on nanocomposite catalysts with a high oxygen mobility (with required mathematical modeling).

Optimized nanocomposite catalysts comprised of Ru+Ni nanoparticles supported on Pr+Sm doped ceria- zirconia solid solution were loaded on heat-conducting substrates (Fechraloy foil and microchannel substrates, Ni-Al foams, etc) and demonstrated a high activity and coking stability in steam/dry/mixed reforming on natural gas into syngas.

This work was supported by FP7 Projects OCMOL and BIOGO and ERA NET RUS PLUS Project NiCe

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The oxidative dehydrogenation of C_2-C_4 hydrocarbons as an alternative way forthe production of light olefins

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The demand for olefins, especially ethylene, propylene and butadiene, is expected to increase significantly in the near future. At the present time, the main sources of olefins are: steam cracking, fluid-catalytic-cracking, and catalytic dehydrogenation. Although these processes are widely used, they suffer from several limitations: thermodynamic limitations on paraffin conversion; side reactions such as thermal cracking; strongly endothermic reactions to which large amounts of heat must be supplied; formation of coke on the catalyst which requires frequent regeneration. With the goal of overcoming these limitations, research is proceeding along some directions, of which the oxidative dehydrogenation (ODH) of alkanes is one of the most promising. ODH allows overcoming thermodynamic limitations, operating at low temperature, and avoiding frequent catalyst regeneration.

Over the past few years, significant steps forward have been made in the study of new catalyst types and reactor configurations for the ODH of ethane. The ethylene yield values reported with some catalysts are comparable to, or even better than, the corresponding values obtained by steam cracking. Various oxide catalysts on the base of molybdenum and vanadium have been used for ODH of ethane. As the catalyst composition become more complex – from individual oxides to the binary ones and mixed VMoTeNbO eventually, ethylene yield increases approaching the acceptable for commercial application value – no less then 70 %. Kinetic study allows specifying the impact of reaction conditions on catalytic performance. Longevity test during 500 h at 400 °C in reaction mixture 15 % vol. C_2H_6 in air have confirmed the stability of the catalyst developed. Within 360-450 °C temperature was determined does not affect the selectivity to reaction products at the equal value of ethane conversion.

The case of propane ODH is different because the best yields reported are still far from being interesting for industrial implementation. The main reason is that the product of ODH of propane, propylene, is more reactive and easily converted into a further oxidation products: acrylic acid, and CO_x. ODH of propane and oxidation of propane to acrylic acid over mixed VMoTeNbO catalysts will be also considered in the study.

This work was supported by the Ministry of Education and Science of the Russian Federation, unique descriptor of application study no. RFMEFI60714X0053

Cu-ZSM-5 catalyst: chemical aspect of synthesis, DeNO$_x$ properties, prospects of their use in diesel exhaust post-treatment system

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The interest of researchers to Cu-substituted zeolites (ZSM-5, SSZ-13, etc.) is caused by their unique properties in DeNOx processes [1-4] and other redox reactions [5]. The activity of Cu-substituted ZSM-5 catalysts in these reactions was found to depend nonlinearly on the copper content [1,2]. Sometimes the catalytic activity of Cu-ZSM-5 with the same copper loading may differ greatly due to various electron states of copper cations [3,4].

Sorption of Cu(II) ions by H-, Na- and NH_4-form of ZSM-5 during the ion-exchange with aqueous and water-ammonia solutions of copper acetate and copper chloride are well described within the Langmuir monomolecular adsorption [4]. Adding ammonia to aqueous solutions of copper salts has a nonlinear effect on the copper content in the Cu-ZSM-5, which is due to hydrolysis, polycondensation, and complexation reactions in the solution [4]. The control for the copper electronic states detected in the ion-exchanged Cu-ZSM-5 by ESR, UV-Vis DR, TPR-H_2 will be discussed.

Cu-containing zeolites are candidate catalytic materials for diesel particulate filters, because Cu-ZSM-5 catalysts combine unique DeNOx properties with good soot oxidation activity. The Cu-ZSM-5 catalyst formulation and especially the copper electronic state were shown to play a significant role in DeNOx behavior as as well soot oxidation.

The structures of Cu(II) ions with the extra-framework oxygen forming in the water-ammonia solutions of copper salts at moderate ammonia concentrations ($NH_4OH/Cu = 6-15$) are more active in the DeNOx [4] than the isolated Cu(II) ions and CuO nanoparticles on the surface of the zeolite crystallites.

The addition of NO into the oxygen containing mixture promotes the soot oxidation over Cu-containing zeolites. The structures of Cu(II) ions with extra-lattice oxygen in zeolite channels and square-planar clusters $(Cu_2O_2)_x$ on the surface of zeolite crystallites was shown to ensure the soot oxidation at low combustion temperatures with high selectivity to CO_2. The structure of the catalytically active centers was not changed during these reactions, and the catalyst did not lose its activity in the selective reduction of nitrogen oxides by propane.

Prospects of the application of Cu-containing ZSM-5 in the diesel exhaust post-treatment systems will be discussed.

This work was supported by the Federal Agency of Scientific Organizations, project #V46.5.6

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Dynamic Vapor Sorption and Inverse Gas Chromatography: The use in catalytic studies

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Dynamic Vapor Sorption (DVS) is a powerful method of solids characterization, based on sample mass change detection during variation of surrounding atmosphere composition and temperature. Most popular variable in surrounding is humidity, which leads to water adsorption/desorption isotherm. The last is widely used to access hygroscopic characteristics of samples, which could influence on shelf life and other important characteristic of products in various industries from pharma and food to building and construction. In DVS method the precisely diluted vapor constantly going through the chamber with the sample, situated on the microbalance pan. The state-of-art instruments can sense mass changes as low as 10^{-7} g and have incredible stability (less 1 μg drift per day), which gives the opportunity to work with low quantities of solid samples greatly accelerating the speed of equilibration.

In general in catalytic studies it is much more interesting to use DVS with different gases and vapors to study the properties of various parts of heterogeneous catalytic systems. If there is no irreversible interaction in sample-vapor system, than the BET formalism can be applied to sorption isotherms to get the specific surface area of the solid. With the help of BJH theory it is possible to get pore volume distribution. In the case of microporous solids, i.e. zeolites, the change of adsorbing molecule size helps to determine dependence of accessible sample surface from probe molecule size, which can be very important for any heterogeneous catalyst optimization. Using the 2-gas/vapor feature there is the possibility of competitive sorption experiments useful for transport properties studies, which are necessary to predict industrial performance of the catalyst. With a little temperature changes energetic characteristics of sorption of various molecules on the support or active centers can be analyzed. Vacuum feature allows not only to evacuate the surface of the catalyst, but also to work at extremely low partial pressures in static or dynamic sorption mode, which is useful for active centers characterization.

If the vapor or gas interacts with solid sample, which can be active center of the catalyst or its support, there are a lot of ways to characterize this interaction. Phase changes can be directly visualized by internal video-cameras, Raman or NIR-probes. The kinetics of irreversible processes can be accessed through mass/time plots at different temperatures or different partial pressures. Some simple catalysis experiments can be also performed, if the catalyst mass changes during the experiment.

Another method for the catalysts or support surface investigation is the Inverse Gas Chromatography (iGC), which in opposite to convenient GC is used to characterize solid materials by their interactions with various gases. The sample is placed in column and the probe gases are passed through it in carrier gas. Varying the probe gas polarity and temperatures and analyzing retention times/peak forms it is possible to calculate the surface energy of the sample or distribution of surface energy. Also it is possible to distinguish dispersive and polar components of surface energy, which are hardly accessible for porous solids or fine powders by other methods. These energies are responsible for adhesion and coating properties of solids important for the many heterogeneous catalytic systems.

The leader in DVS and iGC instrumentation[1] design and manufacturing is an English company Surface Measurement Systems[2], who is not only produce and enhance the instruments for more than 25 years, but also has a largest research and scientific center for these methods.

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2. http://surfacemeasurementsystems.com/

Компания СокТрейд рада представить современное оборудование ведущих мировых производителей для исследования катализаторов и каталитических систем

Реакторы высокого давления из нержавеющей стали и широкого диапазона различных сплавов компании **Parr Instruments, США** отлично зарекомендовали себя во множестве каталитических лабораторий России, для которых название данной компании стало символом надежности и удобства в работе. В настоящий момент в ассортименте продукции компании Parr Instruments присутствуют как простые автоклавы с манометром, так и сложные системы из трубчатых реакторов, например, для проведения синтеза Фишера-Тропша.

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SECTION 1

CATALYST PREPARATION

The effect of specific surface area on the activity of ruthenium catalysts for ammonia decomposition

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Catalytic decomposition of ammonia to produce CO_x-free hydrogen impurity is important for use in fuel cells, producing protective atmospheres and in other cases. Ruthenium catalysts on carbon supports are one of the best catalysts for ammonia decomposition [1]. The specific surface of the carrier affects the distribution of ruthenium and promoters, their dispersion and interaction, i.e., ultimately, on the catalytic performance.

The main aim is to study the influence of specific surface area of support on the catalytic activity of the ruthenium catalyst of ammonia decomposition.

As the carrier was used "Sibunit", (TU 38 41540-95) with a specific surface area of 326 m^2/g. "Sibunit" not quite homogeneous, so it is fractionated by density: in distilled water floats fraction with $\rho<1,0$ (Sib10) – the yield was 2 %, in solution of $Sr(NO_3)_2$ with a density of 1.3 floats fraction with $1.0<\rho<1,3$ (Sib13) – the yield was 25 %, remains fraction with $\rho>1,7$ (Sib17) – the yield was 73 % (fractionation of this fraction in the KI solution with $\rho=1,7$ do not lead to fractionation). The obtained fractions of "Sibunit" were kept in the solution $Sr(NO_3)_2$ with a density of 1.3, so that the receiving conditions did not differ, then washed with distilled water and dried. The obtained fractions of "Sibunit" were characterized by XRD, Raman spectroscopy, specific surface area determined by BET. XRD showed that with increasing density is slightly decreasing interplanar spacing: Sib10 d_{002}=0,348 nm, Sib13 d_{002}=0,348 nm, d_{002} Sib17=0,346 nm. In the Raman spectra of samples recorded intense scattering band at 1595 cm^{-1} (G-band) and 1325 cm^{-1} (D-band), and also a little intense 1173, 2646, 2903, and 3195 cm^{-1} (2D-band), the origin of which may be associated with defective structure of carbon material [2]. With increasing density, the intensity ratio of D-band intensity to G-band (I_D/I_G) decreases from 1.79 to 1.71 for Sib10 for Sib17 i.e., slightly increases the orderliness of "Sibunit". According to the results of XRD and Raman spectroscopy can conclude that the fraction of "Sibunit" structurally identical. However, the specific surface of the obtained fractions of "Sibunit" differs greatly: Sib10 – 439 m^2/g , Sib13 – 389 m^2/g, Sib17 – 256 m^2/g. Therefore, when studying the activity of catalysts prepared on these support, we can eliminate the influence of all factors except the specific surface area of the support. For one composition the active component of 4% Ru - 13,6 % Cs received the specific catalytic activity *W* at 400 °C (ml $NH_3/(m^2 \bullet min)$): Ru^{am}-$Cs^{2.5}$/Sib10 – 0,087; Ru^{am}-$Cs^{2.5}$/Sib13 – 0,097; Ru^{am}-$Cs^{2.5}$/Sib17 – 0,063.

Transmission electron microscopy shows that the size of the particles Ru: Ru^{am}-$Cs^{2.5}$/Sib10 meet with diameters of 3-5 nm, while at Ru^{am}-$Cs^{2.5}$/Sib17 – 3-7 nm. SEM and TEM show that Ru, Cs and Sr are distributed over the "Sibunite" distributed evenly, regardless of the density fractions.

Thus, the specific surface area "Sibunit" significantly affect the activity of catalysts for the decomposition of ammonia.

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Liquid-phase adsorption of oxygen-containing organic compounds over metal-organic frameworks

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Metal-organic frameworks (MOFs) are a new class of crystalline porous hybrid materials assembled by bonding of metal ions or clusters linked with polydentate organic molecules [1]. Their well-ordered tunable porous structures with a wide range of pore sizes and exceptional textural properties make MOFs perspective candidates for a variety of practical applications. One field in which they proved to be interesting is catalysis, for example in the Lewis acid, Lewis base, acid-base concerted, tandem, oxidation, hydrogenation, C-C coupling and other reactions [1].

Few MOFs, namely Cr-MIL-100, Cr-MIL-101 and UiO-66, show exceptional resistance to air, moisture, common solvents, thermal treatment and, moreover, they reveal interesting catalytic performances. Cr-MIL-100 and Cr-MIL-101 consist of Cr_3O-carboxylate trimers bridged by anions of trimesic and terephalic acid, respectively [2,3]. These MOFs have a rigid zeotype (MTN type) crystal structure. UiO-66 consists of $Zr_6O_4(OH)_4$ building blocks connected via terephthalate linkers [4]. These MOFs are able to behave as truly heterogeneous catalysts in various catalytic reactions; no metal leaching into the reaction media occurs due to their high stability.

Adsorption of reagents and products on the catalyst surface is an essential part of heterogeneous catalytic reactions. Since most of reactions catalyzed by MOFs are liquid-phase processes, liquid-phase adsorption over MOFs needs to be characterized. In this work, we obtained liquid-phase adsorption isotherms of various oxygen-containing organic compounds, such as 2-cyclohexen-1-ol, cyclohexanol, propylene glycol, hydroxyacetone, and methanol over Cr-MIL-101, Cr-MIL-100 and UiO-66 using hexane or acetonitrile as solvent. Typically, adsorption isotherms could be rationalized in terms of Langmuir model. Adsorption constants of cyclohexanol and cyclohexenol over Cr-MIL-101 in hexane turned out to be close within the measurement error (44±10 and 41±13 M^{-1}, respectively). Styrene revealed a lower adsorption constant, 28±6 M^{-1}. Toluene was found out not to adsorb over Cr-MIL-101 in hexane. The adsorption constant for hydroxyacetone over UiO-66 in acetonitrile was determined as 42±12 M^{-1}. Strong adsorption of propylene glycol on UiO-66 (adsorption constant of 290±60 M^{-1}) was found.

The acquired adsorption data can be useful to rationalize some features of propylene glycol [5] and cyclohexane [6] oxidation with tert-butylhydroperoxide over Cr-MIL-100(101) as well as propylene glycol oxidation with H_2O_2 over UiO-66.

This work was partially supported by RFBR Grant 13-03-00413.

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Synthesis and Characterization of Nanocrystalline TiO_2 Powder produced via Pulsed LaserAblation

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Titanium dioxide has been extensively studied due to its unique physicochemical properties and diversity of applications [1]. It is well known that optical and photocatalytic properties of TiO_2 significantly depend on the method of TiO_2 synthesis, purification and way of treatment.

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 [2] or vacuum or gaseous media [3]. The purposeful use of different solvents and gases allows controlling the composition of particles produced via initiating various reactions, including oxidation. Thus, oxides of metals [4] and nanoparticles with the a core-shell structure [5] can be obtained using PLA of reactive metals.

In this work we obtained nanocrystalline TiO_2 powder using PLA in liquid medium. A two-step synthesis of the powder was carried out. As a first step, a colloidal solution of metal target in distilled water was obtained by PLA using Nd:YAG laser (wavelength of 1064 nm, frequency of 20 Hz, pulse duration of 7 ns). In the next step the colloidal solution was dried at 60 °C. The obtained superfine dark blue powder of TiO_2 consists of practically spherical particles with mean sizes of 9-16 nm.

XRD data indicates that the phase composition of TiO_2 contains 65 anatase and 35% of anatase and brookite, respectively. The brookite phase content reduced considerably after the heat treatment to up to 400 °C, while rutile phase was not detected. It was found that TiO_2 spectra had an absorption increase in visible region and a small shift of absorption edge in comparison with the materials after the heat treatment. Probably, it was connected with the existence of defect states (e.g., oxygen vacancies) in TiO_2 as well as the presence of small amount of metal titanium in the composition of TiO_2. The number of defect states reduced during the heat treatment, and, according to the XRD data, a complete oxidation of metallic titanium to TiO_2 also took place. Thus, additional absorption bands in the TiO_2 reflectance spectra disappeared after the heat treatment. Photocatalytic activity and sorption capacity was evaluated by degradation of anionic (methyl orange) and cationic (Nile blue) dyes under visible light irradiation. PLA-prepared TiO_x nanopowder demonstrated higher photocatalytic activity in comparison with commercial Degussa P25 TiO_2 catalyst. This good photocatalytic performance may be ascribed to either the existence of defect states in the structure of TiO_2 or the presence of small amount of metal titanium in composition of TiO_2.

This work was supported by the state assignment of the Russian Ministry of Education and Science (Assignment #2014/223, Project code #1347)

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The effect of the platinum content and the precursor on Pt/BEA/Al_2O_3 activity in reactions of benzene/n-heptane hydroisomerization

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The introduction of new ecological technical regulations [1] made refiners to reduce the content of aromatic hydrocarbons (including benzene) in commercial gasoline for their environmental safety. A promising way to reduce the amount of benzene to 1 % vol. is a hydroisomerization of benzene containing cut. This process allows to convert benzene into environmentally friendly cyclohexane and methylcyclopentane. That conversion along with paraffins isomerization leads to reduce benzene level in the gasoline to increase the octane number.

Bifunctional platinum zeolite catalysts may be used as the hydroisomerization catalysts. It is known that zeolites, which are active in the target reactions, are mordenite (MOR) and beta-zeolite (BEA) [2]. Activity of BEA is higher as compared with MOR due to 3-Dimentional system of functional branched micropores [3].

The support was prepared from a mixture of 70 wt.% alumina and 30 wt.% BEA The Si/Al mole ratio of zeolite were 25 and 40. Platinum was incorporated into the calcined supports from cation $[Pt(NH_3)_4]^{2+}$ and anion $[PtCl_6]^{2-}$ forms of precursors. The content of platinum varied from 0.02 to 0.5 wt.%. Catalytic investigation was carried out with a binary mixture of 20 wt.% benzene and 80 wt.% n-heptane in a down-flow fixed-bed reactor under the following conditions: P = 15 bar, T = 200-320°C, LHSV = 2 h^{-1}, hydrogen/hydrocarbons molar ratio = 3.

The effect of the supported platinum amount and platinum predecessor on the samples catalytic characteristics are presented. It is shown, that:

1) the catalyst activity and yield of the target products is directly dependent on the amount of supported platinum;

2) the catalysts in which platinum was deposited from ammine, showed higher activity. It is probably due to the localization of platinum sites. The yields of heptane isomers on samples, which was prepared from ammine, are lower;

3) Variation of Si/Al mole zeolite ratio from 25 to 40 did not significantly affect to the catalyst acidity and, as a consequence, to its catalytic activity;

4) The most efficient catalyst in the benzene/heptane hydroisomerization is the 0.2-0.3 wt.% Pt catalyst whose support consists of 30 wt.% BEA and 70 wt.% alumina.

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Nafion/MO_x nanocomposites as high-efficient solid acid catalysts

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Sulfated perfluoropolymer-mesoporous support nanocomposites can be used as high-effective catalysts in a numerous of fine organic reactions (SFP/support; SFP = Nafion^{TM} (Du Pont), Flemion^{TM} (Asahi Chemical), Fumapem (Dow Chemical) and MF-4SK (St-Petersburg division BIC) [1]). The advantage of these systems is their high stability in corrosive media and high resistance to deactivation by acid sites leaching processes. These samples were characterized by a high concentration of acid sites, which were exclusively Bronsted and had approximately the same acid strength (Ho ~ -11, which is comparable with concentrated sulfuric acid).

Previously composites based on a commercially available sulfated perfluoropolymer (Nafion) and silica support (SAC13) have been successfully applied as the solid acid in a set of heterogeneous catalytic reactions (etherification, nitration, alkylation, etc.) [2]. In this case the silica addition raised the specific surface of the result composite and increased the availability of Nafion`s sulfonic groups by a uniform polymer distribution on the silica surface. SFP-systems deposited on the other supports (ZrO_2, Al_2O_3, TiO_2 etc.) in the heterogeneous acid catalysis had not been investigated yet.

In present study, we provide the new data on the influence of different SFP/support synthesis parameters and the nature of composite precursors on the physical and catalytic properties of the result composite. The synthesized samples 5-20 wt.% SFP on MO_x or carbonaceous material (M = Zr, Si, Al, Ti; over 40 samples) were investigated by set of physical and chemical methods (low temperature nitrogen adsorption, HRTEM, SEM, XRD, SAXS, spin probe EPR, TGA, NH_3-TPD, acid-base irreversible titration, water-uptake measurements etc.). These data allowed us to develop the method of mesoporous nanocomposites preparation. The sample 14 wt.% SFP/ZrO_x was characterized by the highest ion-exchange capacity (up to 2.5 mmol/g) and high thermal stability (up to 300°C) in comparison to other SFP-materials.

The catalytic activity was tested in the liquid-phase acetic acid esterification model reaction (methanol 2:1 mol. excess; 5 wt.% catalyst; 60°C). Initial turnover frequency value (TOF; $N_{MeOAc}\cdot(N_{acid\_sites}\cdot min)^{-1}$) of SFP/$ZrO_x$ composite reached 9.7 (TOF of unsupported SFP sample was 0.8, whereas TOF of commercial available Nafion-silica composite SAC13 gave 7.3).

Furthermore, the catalytic activity of the prepared samples was tested in gas-phase carboxylic acids esterification and aromatics nitration by method described in our previous work [3]. The composites are stable in these reactions (up to 100 h time-on-stream) and achieved close to 99% conversion of the substrate.

This work was supported by RFBR Grant 15-03-08070a.

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Preparation and study of sulfonated carbon materials as solid acid catalysts

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Carbon based materials with grafted sulfonic groups have a high promise in acid catalyzed reactions such as alkylation, etherification, nitration and many others [1]. Such materials as carbon-based solid acid (CBSA) with high density of sulfonic groups could replace sulfuric acid and increase ecological level of such processes. There are three typical ways of CBSA preparation [2]:

1) Simultaneous carbonization and sulfonation of organic or natural compounds
2) Polymerization of monomers with sulfonic groups and subsequent carbonization
3) Direct sulfonation of as-prepared carbon materials

Whereas in the first two cases carbonization processes has temperature limit due to decomposition of sulfonic groups (~250 °C) it means that such CBSA materials has a low and unstable specific surface area values. In the third case for effective sulfonation of the carbons structure it is need to use fuming sulfuric acid. In the case of using usual sulfuric acid such process has a low efficiency. On the other side using fuming sulfuric acid is very inconvenient for technological applications and there is a challenge how it possible to increase efficiency of using usual sulfuric acid for carbons sulfonation processes.

The main idea of this work it is using catalysts for increasing efficiency sulfuric acid for sulfonation processes of carbon materials. The main result of our work it is found possibility to replace fuming sulfur acid on sulfuric acid + catalysts (transition metal oxides) with similar efficiency. In the case of samples has been used several types of carbons such as carbon nanofibers (CNF), carbon nanotubes (CNT) and other carbon supports. It has been found that such catalytic systems (catalyst + sulfuric acid) are allowed to achieve concentration of sulfonic groups in carbons up to 1.3 mmol/g without using fuming sulfuric acid.

Prepared CBSA has been study by physical methods of investigation. It has been found that in such condition CNF are more stable comparing to CNT. During the sulfonation procedure carbon surface are oxidizing and according FTIR data has been proposed that CNT structure are partially destroyed while CNF structure are more stable in such condition. Moreover in the case of CNF due to “fish-bone” type of structure sulfonic groups are located on the terminal aromatic rings. While in the case of CNT carbon layers are forms defects and sulfonic groups are linked to the terminal rings on the edges of these defects. In the case of carbon materials prepared from glucose and cellulose at 400 °C it is found small quantity of sulfonic groups. It can be explained a low ratio in carbon matrix aromatic rings and condensed aromatic fragments. It is well known that aromatic condensed structures are formed at more high temperatures. So we can to vary quantity of embedded sulfonic groups for different types of carbon matrixes.

Finally CBSA materials have been tested in reactions of low-length and fatty carbon acids etherification. It has been observed good results for stability and activity grafted sulfonic groups in these reactions.

The work is supported by the RAS and FASO Russia (project № V.45.3.5.)

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Study of the effect of the carbon materials modification on their electrochemical properties

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Oil depletion, global warming and pollution are the problems related to the dependence of the modern societies on fossil fuels. The development of a renewable energy sources and effective energy storage systems are important challenges which can solve these problems. The fuel cells (FC) and supercapacitors are considered as perspective renewable energy source and storage devices. High surface area carbon materials (CM) are used as the electrodes for these systems. The low corrosion stability of the CM in Pt/C catalysts is due to the cathode potential rise up to 1.4 V upon start and/or stop of the engine when FC are used as power sources for the vehicles. The same carbon materials could be used as electrodes for supercapacitors. In this case CM should possess high electrochemical capacitance. The capacity of about 100-200 F/g obtained in an aqueous electrolyte on the activated carbon electrode was reported in the literature [2]. This capacity corresponds to the specific energy of 20-40 Wh/kg at 1.2 V. This energy is significantly lower as compared to that found in the batteries. Thus the increase in the specific energy for the supercapacitors by improving capacity of the material is the important task at the moment.

In the work we studied the series of high surface are carbon materials (CM). CMs were modified with the carbon, nitrogen and oxygen. The corrosion stability of CMs was studied in the using accelerated “Start/Stop cycling” protocol in 1-1.5 V RHE of the potential range in 0.1 M $HClO_4$ electrolyte. The changes in surface properties of CMs was controlled by a variety of electrochemical methods (cycling voltammetry with the variable scan rates, chronoamperometry at the constant potential, chronopotentiometry at the constant current. The CMs were also characterized by a set of physico-chemical methods (X-ray photoelectron spectroscopy, low temperature nitrogen adsorption). The possible existence of two surface sites of different stability, capacity and resistance was supposed on the basis of the chronoamperometric results. It was also demonstrated that the simple method of the electrochemical activation allowed us to increase significantly the electrochemical capacity of the carbon materials (from ~ 50 to ~ 150 F/g). The effect of the modification of carbon materials with carbon and nitrogen atoms, the effect of the time and temperature of the activation on electrochemical surface properties and performance during electrochemical oxidation is discussed in the paper.

This work was supported by Russian Academy of Sciences and Federal Agency of Scientific Organizations (project № V.46.2.4).

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Bi(III) immobilization inside porous metal-organic framework: toward enhanced photocatalytic performance

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Development of highly efficient photocatalysts is one of challenges of modern inorganic and material chemistry. Applications cover such areas as wastewater treatment, air purification, photocatalytic water splitting for ecological benign production of hydrogen, selective and efficient chemical synthesis. Among the huge class of materials with photocatalytic performance, there is a large family of bismuth oxohalides BiOX (X = Cl, Br and I) attracting much attention due to their structural diversity and high catalytic activity under UV and visible light irradiation. The key factors affecting the catalyst activity are morphology, surface area and size of particles. There are many approaches to control morphology and particle size during synthesis but a difficult problem is to keep that size and morphology intact during catalyst applying. From this point of view, impregnation of photocatalyst into a stable porous matrix offers a suitable solution. Crystalline porous metal-organic frameworks are good candidates to be a catalyst's supports due to huge diversity of topologies, regularity of their structure, high porosity, enough stability and accessibility via simple hydrothermal synthesis.

In this work, we present the original hybrid catalysts based on mesoporous chromium(III) terephthalate $[Cr_3OF(H_2O)_2(bdc)_3]\cdot nH_2O$ (MIL-101; bdc — terephthalate anion $C_6H_4(COO)_2^{2-}$, $n \approx 15-20$) with embedded bismuth(III) particles which reveals superb photocatalytic activity in degradation of organic dyes as model pollutants. MIL-101 is one the most stable metal-organic framework with outstanding porosity: the BET surface area exceeds 3500 m^2/g while pores with volume more than 1.9 cm^3/g are accessible to inclusion such a large guests as polyoxometalates and cluster complexes.

Bi(III)-containing species inside MIL-101 cages was obtained by two step approach including impregnation of metal-organic framework by Bi(III) salt in acidic media with following fixing of Bi(III)-containing particles by ammonia solution. Two different Bi-containing sources ($BiCl_3$ and BiOBr) were used to obtain Bi(III)-X@MIL-101 (X = Cl, Br) with different sensitivity to UV and visible light. It is well known that the substitution of Br for Cl leads to shift of optimal light wavelength of photocatalytic activity to higher values. Only a small amount of bismuth was determined by elemental analysis: from 0.09 to 0.13 Bi atoms per MIL-101 formula unit or about 1–1.5 Bi atoms per mesocage of MIL-101. According to the powder X-Ray diffraction (XRD) MIL-101 structure keeps intact as well as other phases are absent in samples obtained. Interestingly, but according to EXAFS investigations of Bi(III)-Cl@MIL-101 sample bismuth atoms inside MIL-101 do not interact with chlorine atoms as it occurs in layered BiOCl materials. Bismuth atoms in the cavities of the matrix surrounded by six oxygen atoms at distances Bi–O in the range of 2.1–2.9 Å. On the other hand there are only two bismuth atoms at distances below 3.5 Å in the vicinity of each Bi. It is clearly indicates about formation inside MIL-101 of small oxo-hydroxo Bi-clusters containing about 3 metal atoms with terminal aqua-ligands and connected by bridged oxo- and hydroxo-ligands.

The photocatalytic activity of Bi(III)-X@MIL-101 was tested on a degradation of organic dyes. Solutions of methyl red or methylene blue were fully discolored after 30–50 min of intense irradiation by Hg lamp. The kinetics of the processes are described by the first-order law with rate constants 0.037 min^{-1} and 0.11 min^{-1} for X = Cl and Br, respectively. The specific activity of Bi(III)-Cl@MIL-101 exceeds those of pure BiOCl in 5−6 times. The catalysts stability was confirmed by elemental analysis and powder XRD after catalytic tests as well as solutions was examined for no leaching of both Bi or Cr. The stable performance of catalysts was demonstrated in 4–7 catalytic cycles. It was demonstrated that Bi(III)-Br@MIL-101 possesses photocatalytic activity under visible light irradiation while Bi(III)-Cl@MIL-101 is active only under UV light.

This work was partially supported by RF government (Grant No. 14.Z50.31.006, leading scientist Martin Shröder).

Properties of (Pd,Pt)LiAl-layered double hydroxides prepared by mechanochemical method

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Layered double hydroxides (LDHs) are widely used as adsorbents, anion exchangers, basic catalysts and catalyst supports [1]. Application of LDHs as support precursors for dehydrogenation of light and higher paraffins catalysts is a promising. MgAl-LDHs are sufficiently investigated [2]. Stability of the catalysts can be raised by increasing of basicity through an addition of the alkaline metal atoms [3]. Therefore, a synthesis of LiAl-LDHs for increase its basic properties is a challenge. However, production of LiAl-LDHs by traditional coprecipitation method is hindered. Thus, a search of new methods of these systems production is a topical task. One of these methods is a mechanochemical synthesis allowing to obtain of the materials simply, quickly and without ecological problems.

The aim of the work was investigation of properties of the LiAl-LDHs synthesized by mechanochemical method under different conditions (by varying of the initial mixture chemical composition, Li/Al molar ratio, activation time, material of milling bodies). Besides, the active metals (Pd, Pt) were introduced in LiAl-LDHs at the stage of the support synthesis. Pt(Pd)/LiAl-LDHs catalysts were investigated in model reaction of propane dehydrogenation.

The synthesis of LiAl-LDHs was carried out in a planetary AGO-2 mill with the weight ratio of milling bodies to mechanically activated mixture equal to 40:1 (steel or ceramic milling bodies). Activation time was 15, 30 и 60 minutes and centripetal acceleration of milling bodies was 300 and 1000 m^2/s depending on the ball material. $Al(OH)_3$ (gibbsite), $Al(NO_3)_3 \cdot 9H_2O$, $LiNO_3 \cdot 3H_2O$, LiOH, $PdCl_2$ and $Na_2[PtCl_6]$ were the initial components The structure of the synthesized LDHs was examined using X-ray diffraction analysis (XRD), D8 Advance (Bruker). Thermal decomposition of the samples was studied on an STA-449C Jupiter (Netzsch). Textural properties (specific surface area, pore size and volume) of the samples were examined by the low-temperature nitrogen adsorption after their calcination at 550 °C in a volumetric vacuum static setup ASAP-2020, Micromeritics. Catalytic properties of the Pt(Pd)/LiAl in propane dehydrogenation was investigated in a fixed-bed flow reactor under the following conditions: sample weight 0,50 g., 550 °C, atmospheric pressure, H_2/C_3H_8 = 1:4 mol/mol, WHSV of 8 $g/(g_{cat} \cdot h)$.

According to the obtained data the composition of the initial mixture is the major factor in the synthesis of LiAl-LDHs. It was found that each of synthesized systems was to be a polyphase one. The application of ceramic milling bodies makes its possible to obtain the LiAl- LDHs phase under relatively mild conditions (centripetal acceleration 300 m^2/s, activation time 15 minutes). It was demonstrated the possibility of fast one-stage synthesis of the Pt(Pd)/LiAl-LDHs catalysts by mechanochemical methods.

The work was performed using facilities of the Omsk Regional Shared Equipment Center SB RAS and supported by the Russian Foundation for Basic Research (Project No. 15-03-04405).

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Effect of preparation method on structure of metal-organic framework UiO-66

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Metal organic frameworks (MOFs) have been established as a new class of porous crystalline materials with the aim to use them for gas sorption, separation, chemical sensing devices and catalysis [1]. These materials build from combination of linker molecules with metal-oxo clusters as nodes.

Cavka et al. [2] reported the first synthesis of porous zirconium terephtalate UiO-66 in 2008. This material attracted a lot of attention due to unprecedented thermal (up to 540°C) and solvothermal (water, benzene, ethanol and other chemicals) stability among MOFs. It consists of Zr-oxo-hydroxo clusters $Zr_6O_4(OH)_4$ coordinated by terephtalate ligands. UiO-66 is one of the most promising candidates for oxidative catalysis due to unique stability and well-known zirconium ability to activate hydrogen peroxide make. However, still it has not find significant application in this field. One of the most important problem is difficult traditional method for synthesis of UiO-66. It consists in solvothermal reaction between terephtalic acid and high-cost zirconium (IV) chloride, which is highly susceptible in moisture to hydrolysis with formation of zirconyl chloride. It leads to irreproducible results and necessity of argon atmosphere for reaction. The aim of the present work is to investigate the effect of preparation method using zirconyl nitrate as a precursor on structure of metal-organic framework UiO-66.

UiO-66 was synthesized in teflon-lined stainless steel autoclave. Terephtalic acid, $ZrO(NO_3)_2 \cdot 2H_2O$ and calculated amount of modulator were dissolved in N,N-dimethylformamide. Mixture was heated at 120 °C for 24 h. Obtained material was washed with N,N-dimethyaformamide and ethanol. Before characterization materials were degassed under vacuum. All samples were characterized by XRD, IR and low-temperature nitrogen adsorption analysis.

We have successfully developed approach for synthesis of UiO-66 material from $ZrO(NO_3)_2 \cdot 2H_2O$ through HCl excess addition. Highly crystalline porous solid (S_{BET} = 1264 m^2/g) was prepared. BET surface area was close to surface area of UiO-66 material prepared in [2]. XRD data confirmed formation of UiO-66 phase. No unidentified reflections were observed. It was established that HCl amount was important parameter for the formation of material with desired properties. Addition of HCl excess was aimed to replace strong ligands in zirconium coordination sphere on more labile Cl^- ions. In the case of $ZrO(NO_3)_2 \cdot 2H_2O$ terephtalic acid is not tend to replace hydroxyl and NO_3^- ions in zirconium coordination sphere for the formation of required structure. Indeed, while $ZrO(NO_3)_2 \cdot 2H_2O$ was used instead $ZrCl_4$ in standard synthetic procedure [2], amorphous material with low surface area was obtained. Addition of nitric acid led to formation of low crystalline material with slightly increased S_{BET} (546 m^2/g). In the case of using HF no solid was obtained. It can result from stronger fluoride-zirconium interaction. Usage of equivalent amount of NaCl instead HCl results in amorphous precipitate with S_{BET} = 268 m^2/g. Thus promoting effect of chloride ions is not enough for the formation of UiO-66 phase. Hydrochloric acid plays important role in protonation of oxo- and hydroxyl- groups of zirconium precursor. The effect of water amount is also under investigation.

Catalytic activity of synthesized UiO-66 was examined in propylene glycol oxidation with H_2O_2. We managed to obtain hydroxyacetone with selectivity 85 % at 10 % propylene glycol conversion. Catalytic activity of standard UiO-66 was the same.

This work was supported by “The Tomsk State University Academic D. I. Mendeleev Fund Program” grant in 2016 (8.2.07.2015).

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Egg-Shell Cu-Al Ceramometal Catalyst for Water-Gas Shift Reaction

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Using XRD, NMR, SEM with mapping the structure of porous CuAlO/CuAl ceramometall was studied. The CuAlO/CuAl ceramometall is obtained by mechanical alloying Cu-Al mixtures (Cu:Al = 87:13 wt.%) with following hydrothermal treatment and calcination under the air. The microstructure of initial cermets has an egg-shell character with aluminum and copper metallic phases and X-ray amorphous mixed oxides in cores randomly distributed in the oxide matrix. It has been found, that the activity of massive oxide AlCuZn catalyst is higher, because the surface area of ceramometalls is lower. It has been shown, that the activity of the specific metallic copper surface of ceramometalls in WGS reaction is changed nonmonotonically and symbatically content crystallized intermetallic compound Al4Cu9. Mechanical, textural and thermal properties of ceramometals was estimated. It has been found that the ceramometalls has macropores size to tens of microns. These pores promote to high activity of coarse fraction pelleted catalysts in WGS reaction because high diffusion permeability. For this reason the activity of caremometalls is comparable to that of a granular oxide catalyst based on mixed oxides of copper, zinc and aluminum. Mild leaching leads to a significant increase in activity cermets granules.

This work was supported in part by RFBR grant #14-08-00251 and FP7 Project BIOGO.

Study of interactions in silica dioxide and silver colloids obtained by laser ablation method

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Composites on the base of silica dioxide and silver particles, including obtained by laser ablation method, exhibit catalytic activity in the low-temperature oxidation of CO. CO conversion in low-temperature area depends on the composite preparation method, and its redox treatments. Previously, we have shown that the active samples contained interfacial layer consisting of silica dioxide and silver. Its formation involves the interaction of these components.

Laser ablation of the silicon and silver targets in water leads to the formation of the composite particles that contain Si and SiO_2 (with the average size of 7 nm), and silver particles (6 nm). According to the data of UV-Vis spectroscopy, water dispersion of silica-containing particles is stable over time. Dispersion remains stable at water dilution. The silver particles in aqueous dispersions tend to form aggregates, and this is expressed in widening, and long-wave shift of their plasmon absorption peak. However, mixing of the two dispersions leads to the stabilization of silver particles due to the interaction with the components of silicon dispersion.

The measurement of zeta-potential for silver particles showed a result of – 41 mV, and for Si/SiO_2 particles of – 31 mV, i.e. charge interactions between them are excluded. After the mixing of two dispersions the total zeta-potential decreases to – 28 mV, and pH during 2 h was changed from 5.5 up to 12. The dispersion of silica-containing particles may contain soluble silicic acid that were discovered by the formation of a complex with molybdic acid with yellow color. They can either to bind the silver ions that are always present in the dispersion, or to adsorb on the particles surface. Decrease of the pH can be caused by acid-basic interactions.

To prove this, Si/SiO_2 particles dispersion was synthesized in the presence of oxidizer–hydrogen peroxide. The solid phase was separated by ultra-centrifugation. Next the ablation of silver in silica-containing liquid was carried out. Silver particles obtained have a narrow peak of plasmon absorption with the maximum at 401 nm. The dispersions were stable over time because the situation of this peak did not change, but its intensity decreased. Two weeks later the solution completely decolorized. This suggests that soluble silicic acid stabilize the small silver particles, but they stimulate the particles oxidation, and silver transformation into ionic form. The parallel study of the properties of silver dispersions in H_2O_2 revealed that particles are strongly aggregated and not oxidized.

Thus it can be assumed that the silver ions and particles in the dispersion obtained by laser ablation are stabilized by silicic acid, and the formation of interfacial layer may begin in the liquid phase.

This research was funded by the Russian Ministry of Education and Science (state task No. 2014/223, project code 727).

Alumina-supported copper molybdates for soot oxidation

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Catalytic oxidation is an effective way to control the environmental pollutants such as diesel engine pollutions. Bulk mixed transition metal oxides, specifically copper molybdates, show high catalytic activity in the soot oxidation [1, 2]. However, to develop diesel particulate filter based on copper molybdates, the supported catalysts can be used [3]. The present work is devoted to the preparation of alumina-supported copper molybdates and study of their catalytic performance in soot oxidation.

Two series of supported copper molybdates were prepared by the consecutive impregnation of the support with $(NH_4)_6Mo_7O_{24}$ and $Cu(NO_3)_2$ solutions. The first series of the catalysts was synthesized using alumina as the support, while the second one was prepared using the MgO-modified Al_2O_3. The Cu:Mo molar ratio was 1:1 and 3:2 in both series. The obtained samples were calcined at 700ºC. The samples were investigated by the XRD, H_2-TPR and UV-vis DR electron spectroscopy. The catalytic soot oxidation was studied using thermogravimetry (TG) and differential scanning calorimetry (DSC).

According to the XRD data, weak reflections of $Cu_3Mo_2O_9$ were identified in the patterns of the samples of the first series regardless of the Cu:Mo molar ratio. In the case of the second series, the crystalline phases of copper molybdates as well as copper and molybdenum oxides were not found in the samples indicating a high dispersion of the supported oxides.

The H_2-TPR and UV-vis DR electron spectroscopy data additionally confirm the primarily formation of the crystalline $Cu_3Mo_2O_9$ in both samples of the first series due to a strong interaction of molybdenum oxide with the support surface to form aluminum molybdate. In contrast to the alumina-supported samples, it was shown that the using of MgO-modified alumina as a support for the samples of the second series allowed preventing the interaction between supported oxides and alumina support providing conditions to form dispersed $Cu_3Mo_2O_9$ and $CuMoO_4$ depending on the Cu:Mo molar ratio.

The catalytic performances of bulk and supported copper molybdates toward soot oxidation were studied. The influence of the support and catalyst composition on the catalytic properties was discussed.

This research was supported by the Tomsk State University Academic D.I. Mendeleev Fund Program in 2015-2016.

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The use of exfoliated graphite in catalysis and electrochemical devices

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Exfoliated graphite (EG) represents carbon material which possessed low density and high content of mesopores. EG can be pressed without binder that allows to obtain different industrial materials. This feature of EG lies in the basis of graphite foil and sealing technology. These materials have good mechanical properties and are able to keep their form during their operation [1]. EG has a number of unique performances: a wide operating temperature range, high chemical resistance, excellent sealing ability.

EG is obtained from natural graphite, including step of intercalated graphite (IG) synthesis. IG is graphite intercalation compounds (GIC), obtained by the introduction of molecules and ions of substances (the intercalant) into the interlayer space of graphite crystal lattice. IG is heat treated at temperatures of 900-1500 °C. After heat treatment, EG shows extremely low bulk density and high texture characteristics. Materials and gaskets made from EG are stable in air atmosphere at the temperature up to 500-550 °C, in water vapors – to 650 °C, in an inert atmosphere – to 3000 °C. Also, these materials withstand thermal shocks and low temperatures to -240 °C. As a result, these materials are chemically stable, have high heat and electrical conductivity [2].

EG differs by high values of capacitance in supercapacitors due to high specific surface area. It was revealed that the capacitance of supercapacitors based on expanded graphite reached 110 F/g. This is a key factor in the use of these materials as electrodes. It is important that the capacitance of these materials can be considerably increased by applying the metal oxide nanoparticles [3].

This research was devoted to the synthesis of graphite-like material based on expanded graphite with deposited nickel nanoparticles. The synthesis was conducted by the method described in patent [4]. EG with specific surface area of 300-350 m^2/g was impregnated by aqueous nickel salt solution, then it was calcinated in air and reduced in a hydrogen atmosphere. The sample obtained had a specific surface area of 42 m^2/g.

The presence of uniformly distributed nickel nanoparticles was confirmed by scanning electron microscopy (SEM). The size of nickel nanoparticles was ranged from 20 to 40 nm. The spectrum of energy-dispersive X-ray spectroscopy (EDX) showed the content of metallic nickel on the level of 20 wt.% [5].

In conclusion, it was shown that the material, prepared according the above-mentioned technique, can be used for the decomposition process of light hydrocarbons, and as a material for supercapacitors.

The research was financed by the Grant of President of Russian Federation for Young Researchers PhD (MK-5360.2016.8) and this work was supported by Russian Federation President scholarships, project number SP-69.2016.1.

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The influence of method of preparation of bicomponent Ag-FeO_x/SiO_2 catalysts on the catalytic properties in ethanol oxidative dehydrogenation

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Catalytic conversion of bioethanol is one of the prospective ways for synthesis of valuable chemicals (acetaldehyde, ethylene, butanol, hydrogen etc.) [1]. Now bicomponent catalysts such as composition of noble metal (Ag, Au, Pt)/transition metal oxide (CeO_2, Co_3O_4, Fe_2O_3) supported on different carriers are attractive candidates for elaboration of novel high-efficient catalysts. Modern researchers describe the interaction between components in catalyst in terms of so-called synergetic effect [2, 3], which is associated with improvement of the catalytic properties for bicomponent catalysts in comparison with monocomponent metal or oxide catalyst. However, there is no consensus about the nature of synergetic effect. The main aim is to investigate the influence of second component (iron oxide) on the state and catalytic activity of Ag supported catalysts.

In the present work, two series of catalysts were prepared by impregnation of active component solution. The first group (titled as Ag-FeO_x/SiO_2) was prepared by simultaneous impregnation of solution of iron nitrate and silver trifluoroacetate and then the samples were dried at 110 °C with a subsequent calcination at 550 °C for 6 h. The iron amount were varied from 1 up to 10 %, the silver amount was 5 %. The second group of catalysts (titled as Ag-Fe_2O_3/SiO_2) was prepared by consecutive impregnation method. At first silica was precalcined at 600 °C and then the calcined support was impregnated step-by-step via iron nitrate solution and silver nitrate. After each step of impregnation samples were dried at 110 °C and calcined at 550 °C for 4 h in air. All catalysts were investigated by XRD, N_2 adsorption, TPR-H_2, and TEM and tested in oxidative dehydrogenation of ethanol to acetaldehyde (2 % C_2H_5OH, 18 % O_2, 80 % He).

The strong interaction between active components of catalysts Ag-FeO_x/SiO_2 led to the formation of amorphous deposited Fe-silica layer on the catalyst surface and to shifting of their reduction temperatures. The second group of catalysts (Ag-Fe_2O_3/SiO_2) consisted of Ag nanoparticles and hematite phase reduced at appropriate temperatures during TPR H_2 experiment.

Both groups of catalysts were active in oxidative dehydrogenation of ethanol. The highest acetaldehyde selectivity (~ 90 % at 230 °C) was observed for Ag-FeO_x/SiO_2 catalysts in comparison with Ag-Fe_2O_3/SiO_2 (~ 70 % at 230 °C). The high selectivity of Ag-FeO_x/SiO_2 catalysts are suggested to associate with active bicomponent layer structure on the catalyst surface built of small species of delafossite ($AgFeO_2$) phase. The absence of interface contact between components on the surface of Ag-Fe_2O_3/SiO_2 catalysts was responsible for the decrease of alcohol conversion.

This work was supported by The Tomsk State University Academic D.I. Mendeleev Fund Program in 2016.

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Controlled synthesis of Ru/C catalysts by colloidal method

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Colloidal method based on immobilization of colloidal metal NPs over different types of supports is an effective alternative approach to the synthesis of supported metal catalysts with well-defined particles. A precise control over size and shape of NPs at the nanometer scale by varying the synthesis conditions is expected to allow prediction of their catalytic performance as well as to give a possibility to tune material properties with high accuracy and reproducibility. The purpose of the current work is to explore regularities of ruthenium NPs formation via polyol reduction and to determine key parameters for the synthesis of Ru NPs with a controllable particle size allowing further preparation of heterogeneous catalysts for different catalytic application, e.g. aqueous phase reforming (APR) of bioderived sugars and sugar alcohols. The influence of different synthesis parameters, such as reduction conditions, the ratio between Ru and stabilizing agent (PVP), and the Ru concentration on the particle size was studied.

A series of colloidal Ru NPs were synthesized by the polyol method using $RuCl_3 \cdot nH_2O$ and ethylene glycol (EG) as a metal precursor and a reducing agent, respectively [1]. As a general procedure, $RuCl_3 \times nH_2O$ and PVP (mol Ru/mol monomers PVP = 1/1 – 1/50) were dissolved in EG under stirring followed by heating up to a predetermined temperature (170÷198°C). Reduction with $NaBH_4$ reduction was performed by addition of the stoichiometric amounts of the reducing agent under efficient magnetic stirring. Ru NPs formation as well as their stability after immobilization over mesoporous Sibunit, carbon nanofibers of platelet structure and TiC carbide-derived carbon under reaction conditions simulating APR were monitored by a range of physical methods, including UV-Vis, XRD, TEM, XPS. The effect of the PVP/Ru, Ru concentration, reduction temperature and the reducing mode on the mean diameter and size distribution of Ru-NPs was investigated [1]. The particle size prepared by the current polyol technique does not depend strongly on the Ru/PVP ratio and reduction temperature varied in the range 1/1-1/50 and 170-198ºC, respectively, while an increase in the metal concentration in the solution favored NPs growth. The hundred-fold increase in $RuCl_3$ concentration in the solution was shown to result in a particle size growth from 1.7 to 2.6 nm. Faster reduction by $NaBH_4$ at ambient temperature resulted in formation of smaller NPs of ca 1.8 nm compared to those reduced by EG (2.5 nm). A highly concentrated colloidal solution of well-defined Ru NPs (0.1 M) was obtained by the polyol method using PVP as a stabilizing agent in lower excess (mol Ru/mol monomers PVP = 1/5) and used for immobilization over different carbon supports. Two different methods, including *in-situ* and *ex-situ* techniques, were evaluated for the preparation of carbon supported Ru NPs. The hydrothermal stability of differently prepared 3 wt. % Ru on various carbon supports was assessed at APR simulating reaction conditions in aqueous solutions of acetic acid at 220°C under high N_2 pressure. TEM, XPS, XRF, N_2 physisorption were applied for characterization of catalysts before and after tests. In the case of *in-situ* method Ru NPs size was shown to strongly depend on the type of carbon support being influenced by NPs –support interactions while this effect was negligible for *ex-situ* synthesized Ru catalysts. Synthesized catalysts showed good hydrothermal stability. ICP-AES and XRF data confirmed that Ru leaching was negligible.

The SusFuelCat project has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement No 310490 (www.susfuelcat.eu).

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Synthesis of copper molybdates by co-precipitation: peculiarities of phase, structure and texture genesis

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Copper molybdates have found wide applications, including in manufacturing of lasers, electrochemistry, temperature and pressure sensors, etc. [1]. Besides, copper molybdates $CuMoO_4$ and $Cu_3Mo_2O_9$ were shown to be catalytically active in a range of oxidative reactions such as oxidation of soot [2], alkenes [3] and $(CH_3)_2S_2$ [4]. The use of copper molybdates as functional materials required the development of preparation methods. The present work is focused on the study of peculiarities of formation of copper molybdates with desired phase composition, structure and textural characteristics in the course of co-precipitation and subsequent thermal treatment.

The samples were prepared by the co-precipitation method. Water solutions of $Cu(NO_3)_2$ and $(NH_4)_6Mo_7O_{24}$ or K_2MoO_4 (in case of KOH as noted below) were used as copper and molybdenum precursors, respectively. Aqueous solutions of NH_4OH, KOH, NaOH were used as a precipitating agent. The precipitate formed was aged in a mother solution at 25 and 60 ºC. The obtained samples were dried at 80 ºC for 6 h and then calcined at 500 ºC for 4 h. The samples were investigated by a complex of methods such as XRD, STA and MP AES.

According to the XRD, STA and chemical analysis data, in case of NH_4OH precipitant, the formation of a mixture of $(NH_4)_2Cu_4(NH_3)_3Mo_5O_{20}$ and $CuO\cdot 3H_2O$ is observed under the precipitate aging at 25 ºC followed by drying at 80 ºC. The precipitate aging at 60 ºC followed by drying at 80 ºC is accompanied by the formation of a mixture of $Cu(OH)_2\cdot nH_2O$ and $Cu_3Mo_2O_8(OH)_2$. The calcination of the samples at 500 ºC results in the formation of a mixture of $Cu_3Mo_2O_9$ and CuO.

In case of KOH precipitant, the formation of a mixture of $Cu_3Mo_2O_8(OH)_2$ and $K_2Mo_3O_{10}$ phases takes place under the precipitate aging at 25 ºC followed by drying at 80 ºC. Subsequent sample calcination at 500 ºC leads to the formation of a mixture of $K_2Cu_3(MoO_4)_4$ and $Cu_3Mo_2O_9$.

The use of NaOH as a precipitating agent results in the formation of an amorphous phase under the precipitate aging at 25 ºC followed by drying at 80 ºC. The temperature treatment of the amorphous sample leads to the formation of the mixture of $CuMoO_4$ and $Cu_3Mo_2O_9$ copper molybdates.

For both KOH and NaOH precipitants, a single-phase $Cu_3Mo_2O_8(OH)_2$ sample is formed as a result of the precipitate aging at 60 ºC followed by drying at 80 ºC, with a single-phase $Cu_3Mo_2O_9$ copper molybdate being formed in the course of its calcination.

Generally, according to the results obtained, the formation of copper molybdates in the course of co-precipitation can be considered in the relation to classical molecular-kinetic theory, which is based on the ideas of solutions and solubility of the substances and the Gibbs–Volmer concepts concerning the nucleation and growth of the crystals. The formation of the single-phase $Cu_3Mo_2O_9$ copper molybdate occurs via the preliminary formation of $Cu_3Mo_2O_8(OH)_2$ phase. However, the formation of the single phase $CuMoO_4$ molybdate was shown to be hindered by the co-precipitation under the given condition.

This research was supported by the Tomsk State University Academic D.I. Mendeleev Fund Program in 2015-2016.

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Silica gel-based monoliths as a support catalyst

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Replacement of a batch reactor by continuous processes, using monolithic microreactor can make them more effective, safer and produce products with stable properties [1]. For applications as catalyst supports in flow reactors, porous silica monoliths require a combination of connected pores of micron-scale to enable fluid flow plus nm-scale pores to enable high catalyst area and activity. They must also be mechanically strong to withstand the pressures required to drive fluid through them at the required flow rate [2]. Such monoliths are made by the sol-gel technology. The sol-gel method is a widely known method of obtaining silicon dioxide. This method allows to obtain materials of the specific structure and form.

The impact of the synthesis conditions (composition, temperature) on the silica structure, pore size and permeability of the silica supports will be discussed.

Silica meso- and macro-porosity was obtained due to a phase separation method, invented by Nakanishi [3]. Nitrogen adsorption and desorption isotherms were measured at 77 K using a Micromeritics TriStar II 3020 instrument. Mercury porosimetry experiments were carried out with Micromeritics AutoPore 9500 equipment. The total porosity of the monolith samples were determined by weighing the monoliths when dried and when filled with water. The effect of heat treatment and mixture composition on the gel composition will be examined using FTIR spectroscopy using a Nicolet 6700, Thermo Fisher Scientific.

Crack free silica rods featured three types of pores detected by mercury porosimetry and nitrogen adsorption: small pore with diameters 3 nm, originating from the presence of CTAB micelles, larger ones with maximum at 20–40 nm, and large macropores with diameters in the range of 140–160 μm, obtained by PEG-induced phase separation. The monoliths exhibited surface area of about from 40 to 379 cm^2/g, mesopore volume from 0.1 to 1.2 cm^3/g and porosity up to 94 %. The monoliths thus obtained appeared to possess larger macropores compared to those reported before [4].

Due to the presence of flow-through pores of 140–160 μm sizes these reactors can operate at low pressure drops which eliminate the need for the use of high pressure pumps. The relatively large surface area, exhibited by mesopores present in silica skeleton allow to attaching functional groups and metal nanoparticles.

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Changing of the properties of the active component of Pd / γ-Al_2O_3 catalysts consequence the acid-base modification of the support

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The paper investigated the change in the texture and acid characteristics of previously modified alumina support by acetic acid, ammonium fluoride, cesium nitrate or sodium hydroxide. Aqueous solutions of these additives were mixed with pseudoboehmite, followed by calcination at 550 ^{0}C in a stream of air and aluminum hydroxide treated with cesium nitrate at 650 ^{0}C. The obtained samples of alumina were used as the supports, which were subjected to chemisorption impregnation with solution of palladium acetylacetonate in benzene. The palladium content in all samples was 0.5 wt %. Performances of the supported systems were evaluated in the process of hydrogenation reaction of 1,3-butadiene in the laboratory. For this purpose, the catalysts were pretreated at 400 ^{0}C in a mixture of 5% O2 in argon for 2 h, 10 min under an inert atmosphere and then in a mixture of 5% H2 in Ar for 2 h

Study the properties of supports, pre-modified with acid-base additives, showed preservation of the phase composition of γ-Al2O3, according to the results of X-ray analysis. According to the low-temperature nitrogen adsorption analysis, was observed increase of the surface area of modified aluminas, except for the sample containing the cesium atoms, compared with the unmodified γ-Al2O3 (S = m^2/g). This was accompanied by the redistribution of surface area and pore volume with increase percentage part of pore less than 5 nm. Pre-modified support by cesium nitrate had S. = 224 m^2/g. According to the method of temperature programmed desorption of ammonia, the introduction of acid modifiers increases the acidity of the corresponding carriers at the expense of growth of strong acid sites; use of basic additives leads to a decrease total acidity with increase in the fraction of medium and strong acid sites.

Studying the properties of supported palladium particles were carried out technique of temperature reduction with hydrogen and carbon monoxide chemisorption titration, followed by desorption of carbon dioxide. The introduction of acid additives in the synthesis of the support leads to the formation of a larger number of electron-deficient palladium particles. Basic additives contribute to lowering the concentration of strong acid sites of the support and as a result, formation of particles of palladium with a high electron density.

A catalyst based on the not modified support provides the degree of conversion of 1,3-butadiene and up to 56% with selectivity for the target component, butene-1 up to 35%. Samples obtained by modifying support by the basic additives exhibit conversion of 1,3-butadiene to 81% with a selectivity to 1-butene to 37%. Samples of the catalysts prepared using acid additives contribute to the low conversion, to 41%. These samples provide high selectivity to butene-1: 59% for a catalyst carrier that has been pre-modified with acetic acid, and 53% for a sample containing fluorine atoms.

Controlled synthesis of Ru/C catalysts by colloidal method

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Colloidal method based on immobilization of colloidal metal NPs over different types of supports is an effective alternative approach to the synthesis of supported metal catalysts with well-defined particles. A precise control over size and shape of NPs at the nanometer scale by varying the synthesis conditions is expected to allow prediction of their catalytic performance as well as to give a possibility to tune material properties with high accuracy and reproducibility. The purpose of the current work is to explore regularities of ruthenium NPs formation via polyol reduction and to determine key parameters for the synthesis of Ru NPs with a controllable particle size allowing further preparation of heterogeneous catalysts for different catalytic application, e.g. aqueous phase reforming (APR) of bioderived sugars and sugar alcohols. The influence of different synthesis parameters, such as reduction conditions, the ratio between Ru and stabilizing agent (PVP), and the Ru concentration on the particle size was studied.

A series of colloidal Ru NPs were synthesized by the polyol method using $RuCl_3 \cdot nH_2O$ and ethylene glycol (EG) as a metal precursor and a reducing agent, respectively [1]. As a general procedure, $RuCl_3 \times nH_2O$ and PVP (mol Ru/mol monomers PVP = 1/1 – 1/50) were dissolved in EG under stirring followed by heating up to a predetermined temperature (170÷198°C). Reduction with $NaBH_4$ reduction was performed by addition of the stoichiometric amounts of the reducing agent under efficient magnetic stirring. Ru NPs formation as well as their stability after immobilization over mesoporous Sibunit, carbon nanofibers of platelet structure and TiC carbide-derived carbon under reaction conditions simulating APR were monitored by a range of physical methods, including UV-Vis, XRD, TEM, XPS. The effect of the PVP/Ru, Ru concentration, reduction temperature and the reducing mode on the mean diameter and size distribution of Ru-NPs was investigated [1]. The particle size prepared by the current polyol technique does not depend strongly on the Ru/PVP ratio and reduction temperature varied in the range 1/1-1/50 and 170-198ºC, respectively, while an increase in the metal concentration in the solution favored NPs growth. The hundred-fold increase in $RuCl_3$ concentration in the solution was shown to result in a particle size growth from 1.7 to 2.6 nm. Faster reduction by $NaBH_4$ at ambient temperature resulted in formation of smaller NPs of ca 1.8 nm compared to those reduced by EG (2.5 nm). A highly concentrated colloidal solution of well-defined Ru NPs (0.1 M) was obtained by the polyol method using PVP as a stabilizing agent in lower excess (mol Ru/mol monomers PVP = 1/5) and used for immobilization over different carbon supports. Two different methods, including *in-situ* and *ex-situ* techniques, were evaluated for the preparation of carbon supported Ru NPs. The hydrothermal stability of differently prepared 3 wt. % Ru on various carbon supports was assessed at APR simulating reaction conditions in aqueous solutions of acetic acid at 220°C under high N_2 pressure. TEM, XPS, XRF, N_2 physisorption were applied for characterization of catalysts before and after tests. In the case of *in-situ* method Ru NPs size was shown to strongly depend on the type of carbon support being influenced by NPs –support interactions while this effect was negligible for *ex-situ* synthesized Ru catalysts. Synthesized catalysts showed good hydrothermal stability. ICP-AES and XRF data confirmed that Ru leaching was negligible.

The SusFuelCat project has received funding from the European Union's Seventh Framework Programme for research, technological development and demonstration under grant agreement No 310490 (www.susfuelcat.eu).

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SECTION 2

PROMISING CATALYTIC PROCESSES

Influence of ZrO_2 and CeO_2 addition on the activity of CrO_x/Al_2O_3 catalysts in dehydrogenation of hydrocarbons

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Currently, isobutane, other light paraffins and ethylbenzene, have a high impact on the world petrochemical industry. Their dehydrogenation products (propylene, n-butenes, isobutylene, styrene, etc.) are widely used in production of synthetic rubbers, plastics and valuable chemicals. For these purposes, one of the main ways to produce olefins from the corresponding alkanes is a catalytic dehydrogenation. There are many approaches to represent and carrying out the dehydrogenation reactions, including fixed [1], fluidized [2] or moving [3] bed of catalyst, oxidative [4] and non-oxidative [5] dehydrogenation, etc. Up to now, different types of mixed oxides [6-8] have been studied as catalysts for dehydrogenation of hydrocarbons. Pt-Sn and CrO_x supported on Al_2O_3 are the main kinds of materials for alkane non-oxidative dehydrogenation. Application of these catalysts is limited by high cost of Pt and toxicity of chromia. According to literature, chromia catalysts supported on ZrO_2 (with low content of CrO_x) are among the most active systems in non-oxidative dehydrogenation reactions [9]. Besides, due to unique properties, CeO_2-containing catalysts are popular materials for oxidative dehydrogenation reactions [10]. However, low surface area and low stability of zirconia and ceria at high temperatures limit their use. Hence, the development of new Cr-containing catalysts modified with ZrO_2 and CeO_2 with low chromia loading for dehydrogenation of paraffins into olefins is of vital importance. It is proposed that reduction of CrO_x to active phase will be held in the reaction mixture flow instead of reduction pretreatment in hydrogen before dehydrogenation. Thereby, the purpose of the present work is to develop systems on mixed supports and study the effect of ZrO_2 and CeO_2 addition on the state and activity of CrO_x supported on alumina in isobutane dehydrogenation.

Cr-containing catalysts with loading of Cr corresponding to a monolayer (5 at_{Cr}/nm^2) were prepared by incipient wetness impregnation method using water solution of H_2CrO_4. The catalysts were dried at room temperature for 12 h and calcined at 600 °C for 4 h. ZrO_2, CeO_2, $Ce_xZr_{(1-x)}O_2$, Al_2O_3 and ZrO_2/Al_2O_3, CeO_2/Al_2O_3 and $Ce_xZr_{(1-x)}O_2/Al_2O_3$ (0.5 monolayer of zirconia and/or ceria, 5 $at_{Zr(Ce)}/nm^2$) were used as supports. ZrO_2/Al_2O_3, CeO_2/Al_2O_3 and $Ce_xZr_{(1-x)}O_2/Al_2O_3$ supports were prepared by incipient wetness impregnation technique using water solution of $ZrO(NO_3)_2\cdot 2H_2O$ and/or $Ce(NO_3)_3\cdot 6H_2O$ stabilized by citric acid. Catalysts were studied by low temperature N_2 sorption, XRD, TPR, UV-vis spectroscopy and tested in reaction of isobutane dehydrogenation in a fixed bed reactor.

The effect of modification by ZrO_2 and/or CeO_2 on the formation of active cites and activity of Cr-containing catalyst supported on Al_2O_3 in dehydrogenation of isobutane will be presented and discussed on the conference.

This work was supported by the Russian federal target program “Research and Development in the Priority Areas of the Science and Technology Complex of Russia for 2014–2020“ (contract no. 14.578.21.0028, RFMEFI57814X0028).

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Palladium catalysts modified by copper or silver for acetylene hydrogenation

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Ethylene is a valuable product in industrial chemistry. It is used as a monomer for production of polyethylene. Acetylene is a strong poison for ethylene polymerization catalysts. Therefore, selective acetylene hydrogenation to ethylene is used for ethylene purification from acetylene [1]. Palladium catalysts are used for acetylene hydrogenation. To improve the acetylene hydrogenation selectivity, supported Pd catalysts are promoted with a second metal (Zn, Ag) [2-4].

In the current study Pd/C, Pd-Cu/C and Pd-Ag/C catalysts were synthesized. The synthesized catalysts were studied in selective acetylene hydrogenation to ethylene, and their properties were compared. Carbon nanofibers (CNF) and carbon nanotubes (CNT) were used as the catalyst supports. For both types of the supports (CNF and CNT) higher Pd concentration in the catalyst was found to lead to higher hydrogenation activity. However, the selectivity of Pd/C catalysts was found to be different. Pd/CNF catalysts based on carbon nanofibers with stacked structure showed the best results in purification of the acetylene-ethylene mixture from acetylene.

Over 0.08%Pd/CNF catalyst acetylene is subjected to complete hydrogenation at 70 °C. The ethane concentration at the reactor outlet is 0.7 mol.%. To improve its selectivity, the palladium catalyst was modified with copper or silver.

Modification of the 0.08%Pd/CNF catalyst with 0.2 wt.% Cu led to the decrease of the catalyst activity. Hydrogenation of the acetylene-ethylene mixture started at 100 °C. Ethylene conversion reached 50% at 210 °C without any observed ethane formation. Further temperature increase (to 235 °C) made it possible to increase acetylene conversion to 98%. The process selectivity decreased, and ethane concentration at the outlet was equal to 0.4 mol.%.

Modification of the 0.08%Pd/CNF catalyst with 0.3 wt.% Ag led to an increase of its selectivity with an obvious decrease of the catalytic activity. Using 0.08%Pd-0.3%Ag/CNF catalyst, 50 % acetylene conversion was achieved at 90 °C with 99% ethylene selectivity. It was found that modification of the Pd/CNF catalyst with silver results in the formation of Pd-Ag alloys. Their formation is the reason for the decrease of the catalytic activity with a significant increase of the selectivity for such catalysts.

The investigation was performed with the financial support of the Russian Science Foundation (Project No. 15-13-10043).

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Selective CO methanation over Ni/CeO_2 catalysts: effect of chlorine doping, influence of carbon dioxide and water vapor on catalytic performance

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Nowadays fuel cells with polymeric proton exchange membrane (PEM FC) are considered as alternative and clean energy sources. Fuel for PEM FC is hydrogen. The H_2-rich gas (reformate) obtained from catalytic conversion of hydrocarbon fuels with subsequent CO water gas shift reaction usually contains 0.5–2 vol.% CO, which poisons the PEM FC anode catalyst and must be removed to a level below 10 ppm. Selective CO methanation is one of the promising methods for CO removal from hydrogen–rich gas mixtures. However, the reformate typically contains about 20 vol.% CO_2 and 10 vol.% H_2O. In this case undesirable CO_2 methanation and reverse water–gas shift (RWGS) reactions may occur, causing considerable consumption of hydrogen and increasing CO outlet concentration. Therefore, there is a need for highly active and selective CO methanation catalyst that prevent both undesirable CO_2 methanation and RWGS reactions.

In this work we show the results on the comparative study of CO methanation in H_2-rich mixtures (1%CO; 1%CO_2; 1%CO+20%CO_2; and realistic H_2-rich mixture (1%CO+20%CO_2+H_2O)) on well-characterized (BET, XRD, TEM, EDXA, HAADF–STEM and CO-chemisorption) Ni/CeO_2 catalysts.

Ni/CeO_2 catalyst prepared by Ni (II) nitrate precursor was very active in CO and CO_2 methanation, in selective CO methanation in realistic H_2-rich mixture the minimal CO outlet concentration was only 130 ppm at 245 °C. Ni/CeO_2 catalyst prepared by Ni (II) chloride precursor has high selectivity in selective CO methanation [1,2]. The CO_2 methanation is inhibited due to the formation of CeOCl species on the ceria surface [2,3]. However Ni/CeO_2 prepared by Ni (II) chloride precursor is less active than Ni/CeO_2 prepared by Ni (II) nitrate precursor [1-3]. So we try to optimize the chlorine introduction procedure to provide high Ni dispersion over Cl-containing ceria in order to obtain highly active and selective catalyst. We prepared the Cl–containing Ni(Cl*)/CeO_2 and Ni/CeO_2(Cl*) by impregnation of, respectively, Ni/CeO_2 catalyst with an aqueous solution of NH_4Cl and Cl–containg CeO_2 with an aqueous solution of Ni(II) nitrate. All Cl–containing catalysts no matter by which method they were doped with chlorine, showed sufficient performance in selective CO methanation, in contrast to Ni/CeO_2 one. All Cl–containing catalysts showed much higher CO cleanup efficiency and provided CO removal from reformate gas to the level of ≤ 10 ppm. In particular, $[CO]_{out} \leq 10$ ppm and SCO ~90÷50% were reached at 240÷285 °C for Ni/CeO_2(Cl*); at 285÷335 °C for Ni(Cl*)/CeO_2; at ~320 °C for Ni(Cl)/CeO_2.

This work was supported by RFBR Grant 14-03-00457a.

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Synthesis, physico-chemical and catalytic properties of Ni/PrCeZrO catalysts of water gas shift reaction

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Currently, the most cost effective way to produce hydrogen is a steam reforming of hydrocarbons. To increase the hydrogen content, the second stage of the process – water gas shift (WGS) reaction is used which occurs in a broad temperature range and is slightly exothermic. For the intermediate temperature range, the catalysts containing oxides of iron and chromium are often used, while catalysts containing oxides of copper, zinc, aluminum, and chromium are usually applied in the low-temperature range. In recent years, catalysts based on solid solutions of cerium and zirconium oxides, including those doped with rare earth elements are considered to be the most promising.

$Pr_{0.2}Ce_{0.4}Zr_{0.4}O_2$ support was prepared via Pechini method. Ni/PrCeZrO samples containing 5, 7.5, 10, and 12.5 wt. % of Ni were prepared by incipient wetness impregnation of support with the aqueous solution of Ni2+ nitrate salts. Further, Ni/PrCeZrO samples were dried using microwave heating and calcined at 700°C in air for 2 h.

According to XRD data, the initial Ni/PrCeZrO catalysts are comprised of a solid solution of praseodymium, cerium and zirconium oxides with the fluorite structure as well as nickel oxide. The size of NiO crystallites increases with the increase of nickel loading, while the specific surface area of catalysts remains almost unchanged. UV-Vis spectra of catalysts, when compared with the spectrum of support, contain absorption bands corresponding to nickel cations in the octahedral oxygen coordination (Ni^{2+}_{Oh}), being a part of the nickel oxide. According to HRTEM, the support is a well-crystallized $Pr0.2Ce_{0.4}Zr_{0.4}O_2$ oxide with a particle size of about 10 nm. The nickel in Ni/PrCeZrO samples is in the form of oxide particles with a size up to 100 nm.

XRD analysis shows that testing of Ni/PrCeZrO catalyst in WGS reaction leads to an increase in the unit cell parameter of $Pr0.2Ce_{0.4}Zr_{0.4}O_2$ solid solution when compared to the samples prior to reaction. The increase in the cell parameter is consequence of the reduction of Ce^{4+} cations to Ce^{3+} and Pr^{4+} to Pr^{3+}. In addition, samples contain metallic nickel with a particle size comparable to that of NiO in the catalyst before reaction. UV-Vis spectra of samples after reaction show an increase in the background that most likely indicates the presence of metallic nickel particles. According to HRTEM of samples after reaction, the active component is metallic nickel particles coated with a thin layer of nickel oxide.

All studied catalysts exhibit a good activity in the intermediate-temperature range (300-500°C). The experiments proved that the yield of the reaction products and, therefore, the catalyst activity only slightly depends on the loading of active component. It was found that the optimum content of nickel in the catalyst providing the maximum activity was 10 wt. %.

To eliminate the local overheating of the catalyst and decrease the pressure drop in the reactor as required for further up-scaling, this active component was supported on a metal plate made of Ni-Al foam alloy. At a fixed contact time the same level of CO conversion as for the fraction of the active component was achieved with its loading on such support ~ 50 wt.%.

Support by FP7 Project BIOGO and Russian Academy of Sciences and Federal Agency of Scientific Organizations (project V.45.3.8) is gratefully acknowledged.

Novel active nickel- and zinc- modified photocatalysts for hydrogen evolution from aqueous solutions of ethanol under visible light irradiation

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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 organic compounds. An ideal model organic system is ethanol [1]. Earlier we have shown that the most active photocatalysts for this donor system contain ε-$Zn(OH)_2$ and $Cd_xZn_{1-x}S$ phases [2]. J. Ran et al. have demonstrated that $Ni(OH)_2$-loaded $Cd_{1-x}Zn_xS$ samples show high photocatalytic activity and photostability in the organic media [3].

In this work y% $Ni(OH)_2/Cd_{0.3}Zn_{0.7}S$ (labeled as y-$Ni(OH)_2$), y% $Ni(OH)_2$/10% $Zn(OH)_2/Cd_{0.3}Zn_{0.7}S$ (labeled as y-$Ni(OH)_2$-10-$Zn(OH)_2$) photocatalysts were prepared by the impregnation method. The obtained samples were characterized by some methods included XRD, DRS, FTIR, TEM techniques. It was shown that $Cd_{0.3}Zn_{0.7}S$, $Ni(OH)_2$ ($Ni(OH)_2$ and $Zn(OH)_2$) phases contained in the prepared samples. Additionally nickel sulphide was observed due to the features of nickel adsorption at the first stage of the catalyst preparation. We platinized the synthesized materials and tested their catalytic activity. The rate of hydrogen production increased with the content of nickel hydroxide increasing up to 10 wt.% for the y-$Ni(OH)_2$ samples and 40 wt.% for the y-$Ni(OH)_2$-10-$Zn(OH)_2$ samples. The maximum rates of H_2 evolution were 4.13 μmol/min and 4.22 μmol/min for 10-$Ni(OH)_2$ and 40-$Ni(OH)_2$-10-$Zn(OH)_2$ samples, respectively. Above these values of the deposited components, the hydrogen evolution decreased gradually. This behavior of the photocatalytic activity can be caused by the heterojunctions between the support and transition metal hydroxides, NiS phases.

Additionally, we prepared three series of the modified nickel hydroxide and zinc hydroxide photocatalysts which differ in the order of the component deposition. These samples were labeled as y-$Ni(OH)_2$-10-$Zn(OH)_2$-number, where number (1, 2 or 3) indicated the corresponding route of the catalyst modification (1: support → $Zn(OH)_2$ deposition → $Ni(OH)_2$ deposition; 2: support → $Ni(OH)_2$ deposition → $Zn(OH)_2$ deposition; 3: support → simultaneous deposition of $Ni(OH)_2$ and $Zn(OH)_2$). NiS, $Cd_{0.3}Zn_{0.7}S$, $Ni(OH)_2$ and $Zn(OH)_2$ phases were observed for the first and the second series of the photocatalysts. XRD and FTIR methods revealed that the solid solutions of $Ni(OH)_2$ and $Zn(OH)_2$ were formed for the y-$Ni(OH)_2$-10-$Zn(OH)_2$-3 samples. All prepared samples were tested in the photocatalytic hydrogen production from aqueous solutions of ethanol under visible light irradiation and demonstrated high values of the catalytic activity. Besides this, we measured the hydrogen production rate of the most active photocatalysts during six cycles, and every cycle lasted 90 min. All samples saved their catalytic activity. Totally, 86 ml, 87 ml, 75 ml, 69 ml of hydrogen were produced on 10-$Ni(OH)_2$, 40-$Ni(OH)_2$-10-$Zn(OH)_2$-1, 30-$Ni(OH)_2$-10-$Zn(OH)_2$-3, 30-$Ni(OH)_2$-10-$Zn(OH)_2$-2 photocatalysts after irradiation during 9 h.

This work was supported by RFBR Grant №15-33-20458 mol_a_ved.

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Catalytic ozonolysis coal crude benzene

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Desulfurization of hydrocarbon fractions of crude benzene coke industry is an urgent task [1,2].

This paper presents the results of a study of catalytic ozonolysis of benzene fraction separated from crude coal benzene. The choice of raw materials, it is determined that the basic impurities contained in raw coal benzene, such as unsaturated and sulfur compounds, fully in focus head-benzene fraction.

The oxidation process was carried out in a stream of ozone-oxygen mixture in the reactor of the bubbling type at a temperature of 25º C, the ozone concentration of the mixture of 30 mg/l, the reaction kinetics was investigated for 1 hour [3-5]. Ozone received in the generator OGVK-02К (Saint Petersburg) using a barrier discharge, with the measurement of ozone concentrations at the inlet and the outlet of the reactor. The amount of catalyst introduced into the reaction mixture amounted to 1 cm^3, and a particle size of less than 1 mm. Samples of supported on Al_2O_3 catalysts were used, containing as the active components of Mg-Cr, Pd or Pt. Analysis of the composition of the initial crude benzene and reaction products was carried out on the chromatograph Chromatec 5000.2.

Analysis of the data shows that the catalytic oxidation is achieved reducing the content of unsaturated and sulfur compounds. The highest degree of removal of sulfur compounds observed in the presence of the supported magnesium chromite. The conversion of sulfur compounds during the duration of the test 1 hour is 90%.

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Catalytic cracking of heavy petroleum feedstock using WC and Co catalysts

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It is known that heavy oil is about 80% of proven global oil reserves and Russia takes the third place by reserves the heavy oil feedstock in the world after Canada and Venezuela. A depletion of light and medium crude oil deposits makes inevitable a greater involvement of the heavy oil feedstock into processing [1]. Another problem of oil industry is to increase a depth of oil refining via increasing of efficiency of secondary refining processes of oil feedstock (mazut, tar, cracking residues, etc.). Most approaches for obtaining of valuable fuel fractions from heavy oil feedstock are based on the use of catalysts for catalytic cracking and hydrocracking. According to the report [2] in 2011, the total global oil refining capacity was slightly more than 88 million barrels per day and that of the catalytic cracking units was close to 14.7 million barrels per day. Besides, catalytic cracking and ancillary units provided near 45% share of the global gasoline market, and contributed much to the global diesel and light olefins markets as well. The catalyst is one of the key factors for the catalytic cracking process, and various catalysts can have a significant differences in the selectivity and the degree of conversion of petroleum feedstock. As is known to all, catalyst is always one of the key factors for catalytic cracking process and different catalysts could lead to significant differences in product distribution. Moreover, compared with technical reform and plant revamp, replacement of the catalytic cracking catalyst is the most economical and efficient way to obtain a better product distribution [3].

Thus, the objective of this work was to investigate the influence of a catalyst based on coarse powders of tungsten carbide and cobalt on products composition of heavy petroleum feedstock catalytic cracking and the determination of the optimal process conditions in the presence of tungsten carbide and cobalt.

The mazut of Novokuibyshevsk oil refinery (density 0.9870 g/cm^3, a sulfur content of 3.04 wt%., H/C = 1,56) was used as the heavy oil feedstock. Commercial coarse powder of cobalt and tungsten carbide were used as catalysts. The experiments were performed in autoclaves with volume 12cm^3 at temperature 420 °C during 1-1.5h in inert atmosphere of Ar. Catalyst load was 0.05 to 2 wt%. Effectiveness of catalysts was evaluated by products composition and a content of light fractions (from initial boiling point to 350 °C). Fractional composition of liquid products was determined by DSC / TGA in an inert nitrogen atmosphere in the temperature range 20-600 °C. The residual sulfur in the liquid products of the reaction were determined by XRF analysis, H/C ratio was determined using the universal elemental analyzer Vario EL cube.

First time ever was discovered the catalytic activity of tungsten carbide and cobalt in reaction of catalytic cracking of heavy petroleum feedstock. The yields of valuable fuel fractions were 71.1 and 69.4% for WC and Co accordingly. In addition, according to the results of XRF measurements WC have a desulfurization activity – 48% of sulfur was removed from liquid products. Additional experiments were conducted on catalysts reuse (at least 3 times) and the results obtained proved a hypothesis about poison resistance of WC and Co because as it was demonstrated, not only has the catalytic activity not decreased but slightly increased.

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Hydrogen production by autothermal reforming of CH_4 over $Ni/Ce_{1-x}La_xO_y$ catalysts: effect of support composition

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Changes in the structure of production and consumption of hydrocarbons show a steady increase in the role of natural gas as an energy source and raw material for the chemical and petrochemical industry. Proven world natural gas reserves were specified as $187.3 \cdot 10^{12}$ m^3 [1]. Natural gas remains main feedstock for production of hydrogen whose world consumption rate steadily grows. Hydrogen can be obtained directly from natural gas by steam reforming (SR), partial oxidation (PO) or autothermal reforming (ATR). ATR is a combination of PO and SR. It is characterized by reduced rate of carbon deposition and more favorable thermal equilibrium that can be varied as a function of the oxygen feed [2]. The development and modernization of Ni-based catalyst for ATR is the actual problem when the high and stable process performance must be achieved. Metal-support interaction is one of key factors for controlling the properties of supported nanoparticles of active component [3]. So, in this work for tuning the properties of supported Ni nanoparticles the $Ce_{1-x}La_xO_y$ materials with different La content were used as supports. The effect of support composition on textural, structural and redox properties of $Ni/Ce_{1-x}La_xO_y$ materials and their activity in ATR of CH_4 was studied.

$Ce_{1-x}La_xO_y$ ($x = 0\text{-}1$) supports were prepared by polymerizable complex method. The $Ni/Ce_{1-x}La_xO_y$ samples were prepared by incipient wetness impregnation of support with aqueous solutions of nickel nitrate. The nominal content of Ni metal was equal to 10 wt.%. The catalysts were characterized by BET, XRD, TA. ATR experiments were performed in a quartz fixed-bed reactor with a feed composition of $CH_4 : H_2O : O_2 : He$ equal to 1 : 1 : 0.75 : 2.5 under atmospheric pressure, at temperatures 300-950^oC and gas flow rate 200 ml_N/min. Analyses of reaction mixtures were accomplished using a Stanford Research Systems QMS 300 mass spectrometric gas analyzer.

According to XRD data, the type of Ni-containing phase and its dispersion depend on La mole fraction. At $x = 0\text{-}0.8$ the NiO particles are observed while at $x = 0.9\text{-}1$ the formation of $LaNiO_3$ occurs. The mean NiO particle size decreases with an increase of La mole fraction in catalyst composition: from 25 (at $x = 0$) to atomic-dispersed nickel (at $x = 0.5$). The activation of catalysts at 700^oC in H_2/Ar leads to some increase of the particle size; meanwhile the stability of Ni active component against sintering is promoted by La presence in support composition. The reducibility of Ni cations is strongly affected by support composition, and temperature of Ni^{n+} reduction differs in the range of $\Delta T = 300^oC$. From the screening of $Ni/Ce_{1-x}La_xO_y$ catalysts in the ATR of CH_4 it is found that difference in the support compositions is the crucial factor determining the activity of these catalysts. The conversion of methane and H_2 yields increase with a decrease of La mole fraction: at 850^oC H_2 yields are equal to 35, 45 and 55% at $x = 1$, 0.5 and 0, respectively, which correlates with the increase of the reducibility of Ni species as a result of weakening of Ni-support interaction. The additional differences in catalytic activity during prolonged time on stream are discussed in correlation with physicochemical properties of $Ni/Ce_{1-x}La_xO_y$.

The authors are thankful to Dr. V.A. Ushakov, Ms. T.Ya. Efimenko and Ms. G.S. Litvak for their assistance with catalyst characterization. This work was supported by Russian Federal Agency of Scientific Organizations (V45-1-10).

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Study of pretreatment conditions of Cr-containing catalyst of the pentafluoroethane synthesis

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The pentafluoroethane $CHF_2–CF_3$ (hladon R-125) is obtained by gas-phase hydrofluorination of tetrachloroethylene $Cl_2C=CCl_2$ in the presence of chromium-containing catalysts on various supports [1, 2]. The activity and selectivity of the chromium-containing catalyst depends significantly not only on a composition of the catalytic system but also on the activation mode (pretreatment), including heat treatment and hydrofluorination of catalysts precursor. The catalyst is finally formed under the action of fluorine containing mixtures under conditions of a catalytic reaction or fluorinating preactivation.

The aim of this work is to study the influence of fluorinating pretreatment of Cr-containing catalysts precursor on their activity in reaction of the tetrachloroethylene hydrofluorination into pentafluoroethane.

The precursor of catalysts samples was prepared by wet mixing method of powder magnesium fluoride with $CrCl_3 \cdot 6H_2O$. The precursor of catalyst contained 5 wt.% of chromium. The physicochemical properties of the catalytic systems obtained by heat treatment of the precursor in nitrogen and air between 120 and 500°C and their influence on the catalytic activity in tetrachloroethylene hydrofluorination were studied by thermal analyses (DTG, DTA) and specific surface are measurements.

It is shown that by changing the heat treatment conditions can form the precursors not only with different BET specific surface area and chromium containing due to water and HCl removal but with different atomic ratio O:Cr = 1.5-2. Change in atomic ratio O:Cr can be due to the passing of oxidative reaction in temperature range 140-350°C [3]:

$$Cr_2O_3 + 0.5\ O_2 \rightarrow 2\ CrO_2$$

Hydrofluoritation of CrO_2-containig precurcor which heat treated in oxidative atmosphere (air) at 350°C leads to disproportionation of CrO_2 to Cr(III) and Cr(IV) oxides [3]:

$$3\ CrO_2 \rightarrow Cr_2O_3 + CrO_3$$

and then to formation of oxyfluorides with different containing of fluoride atom:

$$Cr_2O_3 + x\ HF \rightarrow 2\ CrO_{(1.5-x/4)}F_{x/2} + x/2\ H_2O$$

$$CrO_3 + 2\ HF \rightarrow CrO_2F_2\uparrow + H_2O\uparrow$$

In results precursor loss 1/3 chromium atoms from their initial content. It is good agreement with ICP-spectroscopy data of chromium content (3.4 wt.%) in catalyst heat treated in air at 350°C and hydrofluorinated.

Activity of catalysis in kinetic regime of the vapor-phase hydrofluorination of tetrachloroethylene were studied at temperature 300-380°C in lab-scale reactor placed into a heat chamber. The reactor was built as a U-type nickel tube (i.d. 0.6 cm) with catalysts volume 6 cm^3. The gaseous product mixture was passed through a scrubber, where acids HF and HCl were converted into CO_2 and H_2O, and then was analyzed by chromatography on-line. The experiments is shown that activity of catalyst heat treated in oxidative atmosphere at 350°C and hydrofluorinated in 2.7-3.5 times at different temperature more then catalysts heat treated in nitrogen.

Influence of fluorinating pretreatment conditions was studied of Cr-containing catalysts precursor of the pentafluoroethane synthesis It is shown that catalyst heat treated in oxidative atmosphere lose about 1/3 chromium atom in fluorinating pretreatment, but have activity in reaction of tetrachloroethylene hydrofluorination into pentafluoroethane in 2.7-3.5 times then heat treated in nitroden.

This work was supported by Russian Academy of Sciences and Federal Agency of Scientific Organizations (project V.44.2.5).

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Creation and testing of active sites on surface complex oxides of BIMEVOX

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The special interest to complex oxides with mixed electron-ionic conductivity is due to their possible use as oxygen-permeable membranes and electrodes of high-temperature electrochemical devices, including fuel cells. Solid electrolytes with perovskite-like structures are good catalysts of oxidation reactions [1] for, e.g., natural raw hydrocarbons conversion [2]. Their activity in oxidation and reduction [3] processes is characteristic of substrates of different natures.

Of great interest are bismuth vanadates belonging to the BIMEVOX family, for which oxygen-ionic conductivity is typical. The catalytic properties of solid electrolytes BIMEVOX family are not well studied. These complex oxides as well as complex phosphates (NASICON family) may be selective catalysts in aliphatic alcohol conversion [4]. In this work the catalytic characteristics of $Bi_4V_{2-2x}Zr_2xO_{11}$-δ were obtained at temperatures up to 350^0C in flow regime with chromato-graphically analysis. The samples were obtained by the solid state synthesis, and were characterized by XRD, IR, XPS. Feature of this work is to create acid centers on mixed oxide surface by the introduction of the PO_4^{3-}anions.

The selectivity of i-butanol dehydrogenation on BIZRVOX was 100%. The aldehyde yield increased linearly when Zr content augment (x =0,05-0,15). In repeated experiment the catalyst activity lowered, but the most active catalyst (x=0,15) was the most stable. The activation energy didn`t depend on x_Zr.

According to IR spectroscopy has been shown to be PO_4^{3-}group is coordinated through cation Zr^{4+}. Phosphate groups resistant to reactionary effect. Promotion of BIZRVOX by phosphoric acid leads to creation of surface acid sites, resulting in a change in the selectivity of conversion of isobutanol and pyridine adsorption.

Thus, the catalytic activity of the modified bismuth vanadate in the conversion of alcohols depends on the nature and amount of Zr ion, as well as on the presence of anion-modified additives, which allow changing the nature of the active centres.

This work was supported by RFBR Grant no. 12-03-31168 and state contract № 10010p/14255 ("U.M.N.I.K.").

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Butanol Dehydration over $Cs_{1-2x}Co_xZr_2(PO_4)_3$ catalysts

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Zirconium phosphates of the NASICON (NZP) type with the basic composition $NaZr_2(PO_4)_3$ are one of the most important compounds in inorganic chemistry. The basic structure of zirconium phosphate is a framework that consists of PO_4 tetrahedra and ZrO_6 octahedra, along with a large number of voids of various sizes and geometries (conducting channels) that can be filled by various polyvalent cations. This can be used to control the strength of surface acid centers and thus the selectivity (direction) of various processes. This is why framework zirconium phosphates with NZP structure are considered promising catalysts of acid–base and oxidation–reduction reactions [1-3].

Zirconium phosphates $Cs_{1-2x}Co_xZr_2(PO_4)_3$ with x=0,15; 0,25; 0,50 were prepared by sol-gel method [4], characterized by physical-chemistry methods (x-ray diffraction XRD, x-ray photoelectron spectroscopy XPS, UV-, IR-spectroscopy, TEM) and tested in decomposition of butanol-2.

The X-ray diffraction data substantiated the structure of NZP. The XPS data showed that the composition of the surface layer differed from the stoichiometric: for example, the concentration of Co2+ on surface of $Co_{0,5}Zr_2(PO_4)_3$ was overrated by a factor of ~2,5.

The main reaction of butanol transformation was dehydration into butens. The triple phosphates samples (x=0,15; 0,25) exhibited the highest activity than double one (x=0,5). The process of ethanol dehydration on framework phosphates takes place through the mechanism of acid catalysis. It was shown correlation of yield of olefins and number of acidic center.

Thus, the cesium-cobalt-zirconium phosphates are promising catalyst of butens production from butanol-2. At the temperatures as high as 400◦C the total alcohol conversion was achieved 60% with selectivity to olefins up to 90%.

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Design of $NiPd/CeZrO_2/Al_2O_3$ catalysts for effective conversion of methane into syngas

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The modern industrial processing of natural gas is directed to the syngas production by steam reforming, autothermal reforming (ATR) or partial oxidation. Increasing amounts of syngas are needed because of its wide application for methanol or Fischer–Tropsch synthesis, hydroformylation reactions, ammonia synthesis or hydrogenation reactions [1]. Among catalytic process of syngas production, ATR is a more power efficient process since it combines endothermic steam reforming and the exothermic partial oxidation reactions. The catalyst used in ATR of CH_4 is Ni supported on different oxides. In order to overcome the disadvantages of this catalyst (deactivation due to the formation of carbonaceous deposits, sintering or oxidation of active component) the optimization of support composition, preparation mode or promotion by noble metals are carried out [2, 3]. The aim of this work was to study the effect of preparation mode and Pd content on the properties of $NiPd/CeZrO_2/Al_2O_3$ catalysts for ATR of CH_4.

The $NiPd/CeZrO_2/Al_2O_3$ catalysts were prepared by combined (Ni+Pd) or sequential (Pd/Ni; Ni/Pd) incipient wetness impregnation of $CeZrO_2/Al_2O_3$ support and calcined at 500°C. The Ni content was equal to 10 wt.% while Pd content was varied in the range 0.05-1 wt.%. The catalysts were characterized by BET, XRD, HRTEM-EDX and H_2-TPR. ATR experiments were performed in a quartz fixed-bed reactor with a feed composition of $CH_4 : H_2O : O_2 :$ He equal to 1 : 1 : 0.75 : 2.5 under atmospheric pressure, at temperatures 650-950ºC and gas flow rate 200 mL_N/min. Analysis of reaction mixtures were accomplished using a Stanford Research Systems QMS 300 mass spectrometric gas analyzer.

According to XRD and HRTEM-EDX, $(\gamma+\delta)$-Al_2O_3, solid solution $CeZrO_2$ (2-10 nm) and NiO (14.0 ± 0.5 nm) are main phases in the prepared catalysts. The high dispersion of active component is preserved after activation of catalyst at 800°C in H_2/Ar: the particle size of Ni-containing phase (Ni^o or NiPd against Pd content) is about 11 nm. From H_2-TPR data it follows that the reducibility of Ni^{2+} can be regulated by catalyst preparation mode and, especially Pd content in their composition. Differences in the structural and redox properties of these series of catalysts correlate with the catalyst performance in ATR of CH_4. It was shown that an increase of Pd content led to a growth of H_2 yield, which may be caused by a decrease of a portion of difficultly reduced Ni^{2+} species. This effect is more pronounced for samples prepared by Pd/Ni sequential impregnation: H_2 yield rises from 45 to 65% at an increase of Pd content from 0 to 1.0 wt.%. At equal chemical composition of catalyst, H_2 yield was affected by the preparation mode. Better process performance is attained in presence of ex-Pd/Ni catalysts. The durability test shows that catalyst performance in ATR of CH_4 and stability against deactivation increase in the following sequence of preparation modes: Ni+Pd < Ni/Pd < Pd/Ni, which can be connected with particular features of Pd distribution. At 850°C the $Ni0.5Pd/CeZrO_2/Al_2O_3$ catalyst prepared by Pd/Ni sequential impregnation provides stable yield of H_2 ~ 65% at 100% CH_4 conversion, which is close to estimated thermodynamic values, confirming its good potential for syngas production by the ATR of CH_4.

The authors are thankful to Dr. V.A. Ushakov, Dr. E.Yu. Gerasimov and Dr. S.A.Yashnik for their assistance with catalyst characterization. This work was supported by Russian Federal Agency of Scientific Organizations (V45-1-10).

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Effect of the structure of sulfur compounds on the catalytic activity of B-Mo/CuZnAlO catalyst in the ODS of diesel fractions

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At present, much attention of researchers is attracted by alternative processes for production of low-sulfur diesel fuel. This is connected with the ever growing requirements to the abatement of sulfur content in motor fuels. One of new desulfurization methods is the process of oxidative desulfurization (ODS) of diesel fractions on catalysts by air oxygen. The advantages of this method are its ability to remove refractory sulfur compounds, such as dibenzothiothene (DBT) and its derivatives under mild conditions and the use of air as a cheap oxidant [1]. Previously, we developed CuZnAlO catalyst (45 wt.% Cu) modified by additives of B and Mo (B-Mo/CuZnAlO), which was found to be promising for the ODS of individual sulfur compounds [2-3]. However the influence of the joint presence of different sulfur compounds on the B-Mo/CuZnAlO catalyst performance was not studied. Therefore the goal of this work was the study of the effect of the structure of sulfur compounds on the catalytic activity of B-Mo/CuZnAlO catalyst at the joint oxidation of such compounds as thiophene (T), DBT and 4,6-dimethyldibenzothiophene (4,6-DMDBT). For the activity tests model fuels based on toluene were prepared, containing ~ 960 ppm total sulfur. The catalyst performance was studied in a flow reactor placed into a furnace with a fluidized bed of quartz sand. The conditions of the tests were: O2/S=120, GHSV=3000 h-1, WHSV=6 h-1, T=300-400oC.

XRD study has shown that B-Mo/CuZnAlO catalyst contains (Cu, Zn)Al2O4, CuO and MoO3 phases. The main ODS process products are sulfur dioxide, carbon dioxide, water and desulfurized fuels. It was established that, independently on the temperature, the sulfur removal efficiency from model fuels was ca. 50%, while the sulfur conversion to gas phase SO2 at temperatures above 350oC attained 99.9%. It was found from the fuel analysis that 4,6-DMDBT and DBT were easier oxidized in comparison with T in the ODS process. The GC-MS analysis of the treated fuels showed the formation of benzene and its alkyl and aryl substituted derivatives as a result of alkylation and aromatic condensation of toluene. In the processes of DBT and 4,6-DMDBT oxidation, in addition to the unreacted sulfur compounds, the formation of intermediate compounds was observed, such as benzothiophene, DBT and 4-methylDBT. No intermediates were detected upon thiophene oxidation. The methods of CHS and DTA-TG-MS analyses showed that the spent catalyst contained sulfur and hydrocarbon accumulated on the catalyst surface and represented by sulfides/polysulfides and sulfates of metals and condensed hydrocarbon.

Thus, it can be concluded that the activity of the B-Mo/CuZnAlO catalyst in the ODS depends on the structure of sulfur compound and increases in the following order: T<DBT<4,6-DMDBT. The sulfur removal from toluene was assumed to take place via the stage of the reactive adsorption of T on the catalyst surface with the formation of metal sulfides and sulfates followed by their oxidation/decomposition with SO2 evolution. The oxidation of DBT and 4,6-DMDBT may occur through the formation of carboxyl groups with the subsequent decarboxylation.

This work was financially supported by ARAMCO under contract No.6600022642 and by Russian Federal Agency of Scientific Organizations (Project V45.1.10)

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Ethylene production through oxidative condensation of methane over $MnMW/SiO_2$ (M = Na, K, Rb) catalysts

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Natural gas can be the starting material for synthesis of most compounds commonly produced by crude oil processing. For effective utilization of natural gas and environmental protection, the development of rational way of methane conversion into value added products is an urgent problem. The oxidative coupling of methane (OCM) is an attractive direct way of methane conversion into C_2 hydrocarbons - ethane and ethylene. The OCM reaction occurs at atmospheric pressure and high temperatures (800-900°C) - typical for processes of methane conversion. The maximum yield and selectivity are 25% and 80%, correspondingly, whereas methane conversion does not exceed 40% [1]. The limit of C_2 yield is connected with the thermodynamically favored nonselective oxidation of hydrocarbons to CO and CO_2 [2]. $MnNaW/SiO_2$ type catalysts were shown to be among the most suitable catalysts for OCM [3]. The composition and synthetic procedure of $MnNaW/SiO_2$ catalysts may have considerable effect on the state and distribution of the active components in the SiO_2 matrix [4]. In this work the effect of preparation conditions on properties of $MnMW/SiO_2$ (M = Na, K, Rb) catalysts was examined. These studies will be applied to elucidate crucial factors, variation of which at the stage of catalyst preparation allows regulation of the OCM reaction parameters.

The $MnMW/SiO_2$ (M = Na, K, Rb) catalysts were prepared by sequential incipient wetness impregnation or mixture slurry method and calcined at 700, 850 or 1000°C. The catalysts were characterized by BET, XRD, TG-DTA, HRTEM-EDX and H_2-TPR. OCM experiments were performed in a quartz fixed-bed reactor with a feed composition of $CH_4 : O_2 : He$ equal to 4 : 1 : 2 under atmospheric pressure at temperatures 650-950ºC and gas flow rate 200 mL_N/min. Analyses of reaction mixtures were accomplished using a Stanford Research Systems QMS 300 mass spectrometric gas analyzer.

It was shown that the synthesis conditions have a significant effect on the catalyst texture and reducibility of the active components, while the type of alkali metal determines the phase composition of W-containing phase. The catalytic tests of $MnMW/SiO_2$ (M = Na, K, Rb) samples in OCM shows that a C_2 yield increases with an increase of catalyst calcination temperature from 700 to 1000°C. The improvement of catalyst performance is also observed: i) at catalyst preparation by the impregnation instead of the mixture slurry method; ii) by selection of a more preferable alkali metal: $K < Rb \approx Na$. Correlations between catalyst performance, preparation method and state of the catalyst were established. The most perspective formulae of OCM catalysts and the rational procedure of their synthesis were selected. The $MnNaW/SiO_2$ catalyst prepared by the impregnation method and calcined at 1000°C was shown to provide ~22% C_2 yield and ~32% CH_4 conversion at 850ºC. The elaborated catalysts are promising for application in resource-saving technologies of ethylene production through OCM.

The authors are thankful to Dr. V.A. Ushakov, Ms. T.Ya. Efimenko, Ms. G.S. Litvak, Dr. E.Yu. Gerasimov and Dr. S.A.Yashnik for their assistance with catalyst characterization. This work was supported by Russian Federal Agency of Scientific Organizations (V45-1-10).

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Structural characterization and photocatalytic activity of nanoctructured anodized Ti-Al powder

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The present paper is focused on (i) structural analysis of TiAl powder anodized in fluoride containing electrolytes before and after air and air-free annealing at 1093 K; (ii) influence of annealing on band gap structure modification and photocatalityc activity of anodic oxide films (AOF) on TiAl powder.

X-ray diffraction, Fourier transform infrared spectroscopy, electron microscopy and atomic force microscopy were used to analyze the structure of these films. The band gap values of investigated powders were determined from their UV-vis absorption spectra. The photocatalytic behavior of anodized TiAl powder was evaluated in the photo-catalytic degradation of methyl orange under UV-vis irradiation technique.

It was shown for the first time, that under optimal anodizing conditions in 10%H_2SO_4+0.15% HF self-organized porous film about 350 nm thick and with effective pore diameter value $<d_p>$= (70±10)nm is formed on the powder particles 'surface. It was established that the oxide film consists essentially of $TiO_2 : Al_2O_3$ in a ratio of approximately 1:1 [1].

The as-anodized oxide films are X-ray amorphous. The crystal structure of air annealed AOF corresponds mainly to the mixture of anatase (for the most part) and rutile as well as Al_2O_3 (α- and γ-polymorph) whereas air-free annealing results in primarily anatase phase TiO_2 and Al_2O_3 (α- and γ-polymorph) and reduced titanium oxides Ti_2O_3, TiO. After air and air-free annealing at 1093K regular nanoporous structure still remains [2].

For the first time it has been established, that the optical band gap for x-ray amorphous heterogeneous oxide formed on Ti-40%Al powder alloy (E_g~2.5 eV) is smaller when compared to titanium dioxide (E_g~3.4 eV). Thus for the developed films photocatalytic activity should be initiated when exposed to radiation with wavelength λ~500-560 nm (which corresponds to the visible light part of the spectrum). It was shown that a steady trend takes place – in presence of anodized powder input concentration of methyl orange declines under both UV and visible light range radiation.

The results obtained are promising for development of new photocatalytic powder nanomaterials.

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Synthesis and properties of photocatalytically active bismuth silicates prepared via hydrothermal method

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In the present time the bigger attention is drawn toward materials possessing advanced photocatalytic properties, better developed particle surface, and higher adsorption. The most commonly used material for photocatalysts is titania, due to its high activity, great chemical stability, non-toxicity and relatively low price [1]. However, it also possesses a variety of notable disadvantages, such as limited absorption spectra and fast recombination of charge carriers.

The scientific interest in the compounds of bismuth (mainly silicates and titanates) has been dramatically increased since recent times. Photocatalysts based on these compounds possess the ability to work in the visible light spectrum, which is undoubtedly beneficial for the matters of energy savings. Varying the phase composition of bismuth compounds and establishing a specific layered structure are key points for achieving notable photocatalytic characteristics [2].

In the following study the samples of bismuth silicate were prepared via hydrothermal treatment. Two series of samples were obtained with $Si(OC_2H_5)_4$ and Na_2SiO_3 as sources of Si with the addition of water in both cases and concentrated HNO_3 in the case of tetraethoxysilane, while $Bi(NO_3)_3$ dissolved in ethanediol was used as a source of Bi in both cases. 100 mL teflon autoclave was employed as a vessel with the molar ratio of 2:1 for Bi and Si, respectively. The temperature of hydrothermal treatment was varied as 150°C, 160°C, and 170°C for both of the series. The resulting substances were calcined at 500°C and 600°C twice being grinded after each calcination procedure.

The properties of obtained samples were investigated via XRD study, UV-Vis spectroscopy, differential thermal analysis, and FT-IR spectroscopy. The photocatalytic activity of the prepared samples in gaseous phase was evaluated in a photodegradation of equilibrium vapor of methanol diluted with air with the catalysts being deposited on quartz with the use of acetylacetone in a procedure similar to [3]. The activity in water solution was evaluated in a photodegradation of methylene blue. Both experiments were carried out with the use of 250W Xe lamp.

According to the results of XRD analysis, the most prevalent phase in the obtained samples is sillenite ($Bi_{12}SiO_{20}$). With this, the first series of bismuth silicates prepared with $Si(OC_2H_5)_4$ also demonstrates a high amount of eulytite ($Bi_4Si_3O_{12}$) in comparison with the second series. However, the photocatalytic activity of the second series proved to be significantly higher in both catalytic reactions with the maximum conversion of methylene blue of 43% after 3 hours of experiment for the sample prepared with the synthesis temperature of 160°C. The best activity in the photodegradation of methanol was also proven by the same sample with the conversion of 27%. UV-Vis spectra showed a significant change in absorption characteristics for the sample prepared at 170°C with Na_2SiO_3 in comparison with the most active sample mentioned above. The first series of the samples, however, didn't demonstrate a notable change in absorption characteristics with the varying temperature of hydrothermal treatment. The reasons of observed effects will be discussed in the report.

This work was supported by the Russian Federal Fund for Assistance to Small Innovative Enterprises (FASIE).

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Diesel fuel catalytic reforming for SOFC feeding

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Extensive research is presently aimed at developing and producing pilot models of compact, efficient, and reliable fuel processors—synthesis gas and hydrogen generators. It is anticipated that such fuel processors will become an integral part of both stationary and portable fuel cell power units. The operation of these processors is based on the catalytic conversion of various fuels into synthesis gas (hydrogen-containing mixtures) followed by the separation/conversion of its components that prevent the efficient electrochemical oxidation of hydrogen in the fuel cell. Promising raw materials for producing hydrogen-containing mixtures are alcohols (methanol and ethanol), ethers, light hydrocarbons (methane, and propane–butane mixtures), gasoline, diesel oil, and biodiesel.

High temperature solid oxide fuel cells are much less demanding towards the fuel type and pretreatment, so it is possible to optimize the process parameters and catalyst composition for reforming of different types of fuel under fairly similar reaction conditions.

The problem of developing catalysts for diesel fuel steam reforming and for the prereforming and reforming of higher hydrocarbons is essentially the problem of creating new, efficient catalysts that would be resistant to coking and to poisoning by sulfur compounds plus the problem of finding reaction conditions minimizing coke formation. Because of the complexity of the diesel fuel composition, most studies in catalyst design and testing were carried out on simpler systems that are variants of model diesel fuels. These include isooctane, decane, dodecane, hexadecane.

The steam reforming of hydrocarbon mixtures, namely diesel fuel satisfying GOST (State Standard) R 52368–2005 (EN 590:2004) has been investigated. These hydrocarbon feedstocks were chosen for the reason that they are universally used as a fuel for various types of power generation units. Experiments have been carried out in a catalytic flow reactor at 500–600°C (for diesel fuel) and pressures of 1–15 atm using a nickel-containing catalyst (NIAP-18). This catalyst has been demonstrated to ensure conversion of different types of hydrocarbon feedstocks into synthesis gas and methane–hydrogen mixtures usable as a fuel for power generation units based on high temperature fuel cells and for spark-ignition, diesel, and gas-diesel engines.

This work was financially supported by Ministry of Education and Science of Russian Federation, Unique Identification Number RFMEFI60716X0149.

Selective one-pot carvone oxime hydrogenation over titania supported gold catalyst

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Dihydrocarvone is a valuable product that has a spearmint-like odor and is used as a flavoring additive in food industry. It is typically formed as a mixture of two stereoisomers and may be obtained starting from hydrogenation of biomass derived carvone using molecular hydrogen over Ni, Pt, Pd, Rh, Ru catalysts. This reaction path requires hydrogenation of a conjugated C=C double bond in the presence of other unsaturated functional groups, such as C=O and an isolated C=C bonds. Application of the above mentioned catalysts typically favors hydrogenation of other unsaturated functional groups, resulting in formation of a complex mixture, with the target dihydrocarvone yield being less than 30%. In our recent work for the first time stereo- and chemoselective carvone hydrogenation to dihydrocarvone catalyzed by Au/TiO_2 catalyst with predominant formation of the *trans*-isomer was reported [1]. This novel approach is of great interest in terms of a possibility to obtain industrially valuable dihydrocarvone via direct carvone hydrogenation. The highest total selectivity to dihydrocarvone (62%) was achieved at a nearly complete carvone conversion (90%) after 13 h, with the *trans*-to-*cis*-dihydrocarvone ratio being about 1.8. As a next step this study is focused on one-pot process consisting of sequential transformations of carvone oxime which is a key intermediate in carvone synthesis from limonene to dihydrocarvone. The aim of this work was to study regularities of carvone oxime transformation over Au/TiO_2 catalyst focusing on exploring feasibility of the one-pot synthesis of dihydrocarvone starting from carvone oxime.

The reaction was carried out in a batch reactor at 100°C under hydrogen pressure of 9 bar over 1.9 wt. % Au/TiO_2 catalyst using methanol as a solvent. Dihydrocarvone synthesis was shown to occur via carvone formation with the subsequent hydrogenation of its conjugated C=C double bond [2]. Application of Au/TiO_2 catalyst for both deoximation and selective hydrogenation of olefinic C=C functional group is reported for the first time. Combination of these steps provides optimization of the synthetic method for dihydrocarvone production from carvone oxime which is a key intermediate in carvone synthesis from limonene. Although the reaction rate is lower than in the case of carvone, a significant increase in the stereoselectivity towards trans-dihydrocarvone was observed for carvone oxime hydrogenation. The ratio between *trans*- and *cis*- dihydrocarvone was close to 4.0 compared to 1.8 achieved in the case of carvone hydrogenation. Application of gold catalysts for dihydrocarvone synthesis from carvone oxime in particular and to control in general consecutive chemoselective hydrogenation of different functional groups seems to be a promising approach due to high selectivity.

This work was supported by RFBR Grant 15-33-20198.

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One-pot amination of biomass-based alcohols over gold catalysts for the synthesis of biologically active compounds

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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 which are extensively applied in food and perfumery industry as flavors, fragrances and spices. Moreover, terpenoids often have biological activities and are used for medical purposes. Terpenoids utilization as platform molecules can provide new opportunities for synthesis of efficacious chemicals in human disease therapy and prevention. We have previously shown that gold catalysts are rather active in one-pot natural terpene alcohol myrtenol amination leading to predominant hydrogenation in the last step of C=N bond instead of a more reactive C=C group of myrtenol [1]. 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 correlation between catalytic activity, substrates structure, support nature and interactions of Au with other metals.

A series of nanosized gold catalysts including Au, AuPd and Pd deposited over different metal oxides (ZrO_2, MgO, Al_2O_3, CeO_2, La_2O_3) were synthesized and tested in one-pot natural monoterpene alcohols amination with equimolar amounts of the substrates without any additives at 140-180°C under nitrogen pressure of 9 bar. The catalytic performance in each step was found to be strongly dependent on the acid-base properties of the support requiring a certain balance between different sites for efficient alcohol amination [1]. Among tested catalysts zirconia-supported gold catalyst with both acidic and basic surface sites afforded optimum consecutive myrtenol transformations resulting in complete conversion of myrtenol and selectivity to the target amine of ca. 53%. The basic sites on the metal oxides surface were suggested to be required for the initial alcohol activation, while availability of protonic groups was important for the target amine formation. At the same time it was found that catalytic activity and selectivity can be also regulated by the catalyst redox pre-treatment [2]. Differences in activity and selectivity for pre-reduced and pre-oxidized catalysts were proposed to be mainly related to a different degree of the support basic properties modification by residual ammonia. The reaction kinetics was studied in detail and modelled based on the mechanistic considerations with the non-catalytic and catalyst deactivation steps introduced into the mechanism [3]. The substrates structure was also varied to obtain potential biological active compounds and to study their physiological properties.

This work was supported by RFBR Grant 16-33-60028.

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The influence of producing method of magnesium fluoride on its photo- and X-ray sorption properties

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The interest to study the particularities of oxygen photo- and X-ray sorption development on the surface of magnesium fluoride of different ways of obtaining is determined by the fact that photosorption activity of magnesium fluoride situated far behind the edge of self-adsorption band is connected with contaminations exciting. In this paper finely-divided samples of magnesium fluoride being of kind “pure for optical ceramics” obtained from MgCl2 - (MgF2-1), and samples of kind “pure for thermal pressuring” formed from basic magnesium carbonate – (MgF2-2) have been studied. The acid surface in connection with acid-basic properties is typical for the samples of (MgF2-1) pHiip and pHiis = 4,0-4,6, Ho=3,5, while that for (MgF2-2), is the neutral one pHiip and pHiis = 6,5-7,3; Ho=6,0 [1, 2]. pHiip - pH of izoionic point determined by the ΔpH – pHo ratio; pHiis – pH of isoionic state determined by the equal pH value of water MgF2 slurry), H0 - acidity function Gamete , determined from indicator method [3] .

Photo- and X-ray sorption of oxygen nave been examined on the samples mentioned above. Illumination of the samples has been carried out with the help of full light of PRK-lamp. The portative apparatus REIS-I (a tube with copper anode) has been used as a source of X-ray radiation.

The ions of contaminated oxygen as well as F- and M- centers are considered to be possible centers of photostimulated oxygen adsorption on the samples studied. It has been suggested that high temperature forms of (530 and 650 K) can be a result of dissociative adsorption of oxygen while low temperature forms (430 and 440 K) can be referred to the molecular forms of O2–t types [4]. Photosorption capacity of the samples obtained by different ways is similar.

Spectra of thermodesorption after photosorption for (MgF2-1) and (MgF2-2) are similar according to the position of peaks and their intensity. Meanwhile in the spectra of oxygen postsorbed from “chloride samples” the intensive low temperature maximums (420 K) have been observed. For “carbonate samples” peaks of less intensity with more equal distribution of intensity up to 780 K have been registered.

Kinetics of oxygen photosorption for all the samples has a power-law character. Kinetics of oxygen X-ray sorption on magnesium fluoride can be easily described with an equation of “local” kinetics. Spectra of X-ray-sorbed oxygen thermodesorption sharply differ from TD-spectra of oxygen photosorbed on these samples. This fact also confirms the different mechanism of these processes development [1].

It is noticed that magnesium fluoride samples obtained from basic magnesium carbonate have neutral surface and more stable in acid-base and photo- and X-ray properties.

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Oxidation of glyoxal to glyoxylic acid over Pt-CeO$_2$/C catalysts

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Glyoxylic acid and its derivatives are used in manufacturing of important products at different branches of industry, from cosmetology to pharmaceutical industry. Glyoxylic acid can be produced from glyoxal or ethylene glycol by oxidative treatment with a nitric acid, which gives harmful NO$_x$ gases as by-products [1]. Electrochemical and fermentative methods of producing the glyoxylic acid are also known [2]. A catalytic liquid phase oxidation allows avoiding the use of aggressive acids, enzymes or elevated temperatures and pressures; moreover, the catalysts can be reused many times. Platinum group elements are active in aldehyde oxidation reactions, and Pt is the most selective toward the corresponding acids [3]. According to [4], ceria as a modifier increases the activity and selectivity of the Pt/C catalyst. Thus, development of new catalysts for selective oxidation of aldehydes into corresponding acids is of importance.

The aim of the present work is to study the liquid phase oxidation of glyoxal into glyoxylic acid over the Pt-CeO$_2$ catalysts supported on different active carbons.

Sibunit C-1 and hemosorbent CKN 2K were selected as supports for the Pt catalysts. Carbons were activated with 2N HCl and by the oxygen treatment at 500 °C. To prepare the Pt/C catalysts, modified by CeO$_2$, carbon supports were impregnated with aqueous mixture of H_2PtCl_6 and $Ce(NO_3)_3$. The precursors of the active components were hydrolyzed by 10 % solution of NaOH and reduced in formaldehyde at 80 °C. After that the samples were filtrated, washed by water for pH 7 and dried at 50 °C for 24 h. The oxidation of 0.1 M glyoxal aqueous solution (40%, SIGMA-ALDRICH) to glyoxylic acid was carried out in a round-bottomed flask. The catalytic tests were carried out for 5 hours with an atmospheric oxygen at the pH of 7-8 at 20 and 40 °C. The reaction medium should have a pH value close to 7.7. In an alkaline medium, a mixture of glycolic and oxalic acids is formed through the Cannizzaro reactions. In the acidic medium oxalic acid is mainly produced because the second aldehyde group is oxidized [3, 5].

Pore structure and specific surface area of the supports and catalysts were investigated by low-temperature nitrogen adsorption using a 3Flex analyzer (Micromeritics, USA). The phase composition of the catalysts was studied by the X-ray diffraction. The feed and reaction solution were investigated by the gas chromatography and a high performance liquid chromatography.

It was shown that the activation of the carbon supports by the hydrochloric acid led to decreasing of specific surface area and increasing of the average pore size. It was shown by the XRD that both Pt and CeO$_2$ were stabilized in a highly dispersed state with average particle sizes of 5-7 nm and 3.3 nm, respectively.

Both Pt-CeO$_2$/C catalysts showed high catalytic activity and selectivity toward glyoxylic acid of 60-75 %. The activity of the Pt-CeO$_2$/hemosorbent was higher than the one for the Pt-CeO$_2$/Sibunit due to higher specific surface area and porosity. Increasing the temperature of the catalytic reaction from 20 to 40 °C led to conversion growth without selectivity changes.

Thus, the liquid phased catalytic oxidation of glyoxal into glyoxylic acid over Pt-CeO$_2$/C catalysts can be considered a promising ecofriendly way to obtain the acid without NO$_x$ emissions.

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Influence of Cu- and Zn-based modifiers on the activity of CrO_x/Al_2O_3 catalysts for dehydrogenation of light hydrocarbons

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Dehydrogenation of saturated hydrocarbons (paraffins) into olefin hydrocarbons is among the most important petrochemical catalytic processes. C_3-C_5 olefins, in particular, isobutylene, are widely used in production of synthetic rubber, membranes, fibers, fuel additives, plastics, etc.

CrO_x/Al_2O_3 catalysts are used for industrial dehydrogenation of saturated hydrocarbons into corresponding olefins. However, the catalyst deactivation caused by coke formation is the main problem of the CrO_x/Al_2O_3 catalysts. The catalyst modification by alkali metals and other elements is the main way to increase the selectivity and stability of these catalysts. The aim of this work is to study the influence of copper- and zinc-based modifiers on the state of chromium oxides and catalytic properties of the CrO_x/Al_2O_3 catalysts in the dehydrogenation of isobutane to isobutylene.

A series of CrO_x/Al_2O_3 catalysts, unmodified and modified with copper and zinc compounds, were prepared by successive impregnation method, "one-pot" impregnation and sol-gel synthesis [1]. Activated aluminum oxide $Cu(NO_3)_2*3H_2O$ and $Zn(NO_3)_2*6H_2O$ were used as precursors. CrO_3 and KNO_3 were used as precursors of active component and alkaline promoter, respectively. The prepared samples were characterized by the low-temperature N_2 sorption, XRD, H_2-TPR and UV-vis spectroscopy. The catalytic activity of the samples was studied in the dehydrogenation of isobutane to isobutylene in a fixed bed reactor.

It was shown that the preparation method determines the state of the active component and the catalytic properties of the Cu- and Zn-modified CrO_x/Al_2O_3 catalysts in the dehydrogenation of isobutane to isobutylene. Using the UV-vis spectroscopy, H_2-TPR and XRD methods it was revealed that the active component is mainly distributed on the support surface in two main states, namely, Cr^{6+} and Cr^{3+}. The sample prepared by successive impregnation had the highest conversion (14.2 %) with selectivity of 98.9%. Low conversion for the sample, prepared by "one-pot" method, was due to formation of the sites responsible for non-selective conversion of isobutane (e.g., $ZnCrO_4$, ZnO, etc. [2]). The sample obtained by the sol impregnation had the lowest isobutene conversion, associated with a decreasing of Cr^{6+}/Cr^{3+} ratio over the catalyst surface. On the basis of the comparative studies of unmodified samples and those modified with individual or both Cu and Zn modifiers, the synergistic effect determining the distribution of the active component on the catalyst surface was shown for the samples modified by both Cu and Zn modifiers. It was found that under the influence of reaction mixture a sequential reduction of the highly dispersed copper species participating in the formation of active and selective Cr-containing sites occurs on the catalyst surface. The role of the Zn-based modifier was probably connected with a decreasing of the processes leading to the formation of catalytically inactive copper- and/or chromium sites on the catalyst surface.

Thus, the simultaneous introduction of Zn- and Cu-based modifiers results in an increasing of the activity and selectivity of CrO_x/Al_2O_3 catalysts in the isobutene dehydrogenation. The Zn- and Cu-based modifiers provide the formation of active surface of the CrO_x/Al_2O_3 catalysts under the action of redox conditions of the catalytic process. The approach proposed can be used to produce novel highly effective and stable catalysts for the dehydrogenation of light paraffins into the corresponding olefins.

This work was supported by the federal target program "Research and Development in the Priority Areas of the Science and Technology Complex of Russia for 2014–2020" (contract no. 14.578.21.0028, RFMEFI57814X0028).

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New Effective Polyamine-Based Pd Catalysts for Selective Hydrogenation of Acetylene Alcohols

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Selective hydrogenation of acetylene alcohols is widely used in fine organic synthesis in production of fragrances, biologically active compounds and fat-soluble vitamins [1]. Palladium is well known to be the most selective catalyst for hydrogenation of triple -C≡C- bond of alkynols. Historically, Lindlar suggested $Pd/CaCO_3$ catalyst modified with lead acetate and quinoline, which allows up to 95% selectivity at nearly 100% conversion in triple bond hydrogenation [2]. However, the application of these modifiers leads to pollution of target products. The use of polymeric matrices as supports allows achieving high activity and selectivity without the necessity of the use of toxic modifiers as well as providing the possibility of stabilization of Pd-containing species inside polymer nanostructures.

Functionalized polymers were shown to be the most promising ones from the point of view of provision of high metal dispersion, improvement of reactant diffusion into the pores and facilitation of interaction between polymer and metal nanoparticles (NPs) [3]. Recently it was shown, that Pd NPs stabilized in hyper-cross-linked polystyrene bearing amino-groups allows achieving high selectivity in triple bond hydrogenation (more than 98% at 95% conversion of acetylene alcohol – dimethylethynylcarbinol (DMEC)) [4]. It is noteworthy that free electron doublet of nitrogen in the amino groups can be involved in binding of Pd^{2+} ions from the precursor solution that likely results in more uniform distribution of Pd precursor inside the polymer along with prevention of Pd leaching. Besides, more rapid reduction of Pd^{2+} ions to Pd^0 with formation of Pd NPs can be found.

In the framework of this study the series of Pd-containing catalysts based on polyamines (1%-Pd/PA) was synthesized via conventional wet-impregnation method at variation of PA type (molecular weight, existence of additional functional groups (-OH, -COOH, $-PO(OH)_2$, etc.), cross-linking degree hydrophobicity/hydrophilicity) while using Pd acetate as a precursor. All the synthesized catalysts were tested in hydrogenation of DMEC (intermediate product in the synthesis of fragrant compounds (such as linalool, linalyl acetate, citral, citronellol etc.) and vitamins A, E and K). Catalytic testing was carried out in a batch mode in 60 mL isothermal glass batch reactor at a temperature of 65°C. Ethanol was used as solvent. Before the addition of DMEC, in each experiment catalysts were reduced *in situ* with hydrogen at reaction conditions during 60 min. Samples were analyzed via GC-MS (Shimadzu GCMS-QP010S).

It was shown that the use PA as supports led to noticeable increase in selectivity (more than 99% at 98% of DMEC conversion was achieved) at reasonable activity, which was comparable to industrial Lindlar catalyst, at lower metal loading. It is noteworthy that the variation of PA nature had strong influence on the catalytic behavior: best results were found for hydrophilic polymer having highest degree of cross-linking.

This study was funded by the Russian Science Foundation, project 15-19-20023.

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Hydrogenation of 2-chloro-4-nitrobenzene over supported palladium, platinum and iridium catalysts and skeletal nickel in aqueous solutions of 2-propanol

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Chloroaminebenzene is a significant chemical that is used extensively in organic synthesis of different industrial important compounds. The liquid phase hydrogenation is perspective method of halogen substituted amine production. But high degree of dehalogenation decreases product yield of end product. Therefore, the selection of catalytic system composition requires thoroughness. Analysis of literary data argues, solvent is determinative factor of selectivity for chloroamine as well as catalyst.

The purpose of investigation is study of 2-chloro-4-nitrobenzene hydrogenation kinetics over supported palladium, platinum, iridium catalysts and skeletal nickel in aqueous solutions 2-propanol, comparison between degree dehalogenation, content of 2-propanol and solvation ability of solvent.

The hydrogenation of 2-chloro-4-nitrobenzene was performed in the temperature-controlled semi batch stirred reactor. The stirred reactor allows to perform of process without the effect of external diffusion. The palladium, platinum and iridium supported over "AR-V" granulated active carbon were utilized as catalysts with different content of metal.

The isopropanol and ethyl acetate was used as solvent. The reaction was monitored using hydrogen uptake and samples were also removed at regular time intervals and analyzed using a UV Vis scanning spectrophotometer «LEKI SS 2110 UV» and a potentiometric titration method.

According to the obtained results, degree dehalogenation 2-chloro-1,4-phenylenediamine increases simultaneously with increases mole percent of water in solvent and dielectric constant of solvent. Also, this regularity is correct for individual solvents.

The carried study showed the sequence of reaction rates corresponds to order Pd > Pt >> Ir. It is well known that skeletal nickel widely applied in liquid phase hydrogenation. Herewith, skeletal nickel may be analog of platinum and palladium. Supported palladium catalyst behaved similarly to skeletal nickel with decreasing of palladium content.

It is well known that skeletal nickel widely applied in liquid phase hydrogenation. Herewith, skeletal nickel may be analog of platinum and palladium. Hydrogenation of 2-chloro-4-nitrobenzene over 0.5% supported palladium catalyst behaved similarly to hydrogenation over skeletal nickel.

The catalyst samples, 10 % Pd/C, 0.8% Pd/C, 0.5% Pd/C were examined using high-resolution scanning electron microscope Mira 3LMH (TESCAN, Czech Republic), equipped with a detector of the reflected (SE) and back scattered electrons (BSE). The obtained images yielded information about absence of catalyst surface changes after using in reaction.

The optimal selectivity of 2-chloro-4-nitrobenzene hydrogenation for 2-chloro-1,4-phenylenediamine correspond to 1 % Pt/C и 1 % Ir/C. Dehalogenation of 2-chloro-1,4-phenylenediamine did not observe over these catalysts.

Conversion of cellulose into ethylene-and propylene glycol

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Cellulose is a naturally occurring biopolymer of glucose with 1,4-glycosidic linkages. As the most abundant non-ediblebiomass in nature, cellulose is considered to be a viable alternative to fossil resources for the sustainable production of fuels and chemicals. The routes to glycols have attracted particular attention due to their high atom-economy and energy-efficiency as well as the versatile uses of polyols as fine chemicals directly and as precursors for the synthesis of fuels and especially value-added compounds [1].

Ethylene glycol (EG) and propylene glycol (PG) are the most important chemical raw materials and widely used in the manufacture of pharmaceuticals, liquid fuel, emulsifiers, surfactants, antifreeze agents, lubricants and solvents, as well as for the synthesis of polyester fibers and resins, such as poly (ethylene terephthalate) and poly (ethylene naphthalate). PG is also used for the synthesis of lactic acid, which is widely used, particularly in the production of biodegradable polymers (polylactones). Since the modern production of glycol based non-renewable petroleum feedstocks and different environmental cleanliness, is urgent to develop new efficient and environmentally friendly ways to produce PG and EG from pulp stocks which are renewable and are large enough to completely cover the chemical industry needs these glycols.Development of effective methods for a plant biomass conversion for the needs of the chemical and fuel industries, is currently of special interest, particular attention is paid to the production such as EG and PG. For this purpose cellulose is one of the most promising types renewable sources [2].

Ru-containing heterogeneous catalyst systems are the most active in the conversion of cellulose.[2]New possibilities are opened by the use of magnetic separable catalysts based on magnetic nanoparticles (MNPs) [3]. MNPs-based catalysts have a number of advantages due to easy separation from the reaction mixture by external magnetic field.

The main objective of this study is investigation of the process of cellulose hydrogenolysis in subcritical water in the presence of Ru-containing catalyst based on magnetic iron oxide nanoparticles - 5% Ru-Fe_3O_4-SiO_2 and the selection of optimal process conditions to ensure maximum yield of glycols.

The experiments were performed in a steel reactor (50 cm^3, Parr Instrument, USA). Microcrystalline cellulose, a catalyst and 30 mL of distilled water were loaded into the reactor. Then reactor was flushed three times with hydrogen under 60 bar pressure.The mixture was heated and stirred at 100 rpm. After reaching the operating temperature the stirrer speed was increased up to 600 rpm. This moment was chosen as the reaction starting time.At the end of the experiment the catalyst was separated by neodymium magnet. The non-hydrolyzed cellulose was separated by filtration.

Ru-containing magnetically retrievable catalysts on the basis of Fe_3O_4-SiO_2 MNPs allow converting microcrystalline cellulose into EG and PG with the selectivity 19 and 20%. The optimal conditions of the process are temperature 255 °C, hydrogen partial pressure 60 bar, the duration of the process 50 minutes, 0.1167 mmol ruthenium as a component of the catalyst per 1 g of cellulose; $Ca(OH)_2$ as a cracking agent in an amount of 0.195 mol per 1 mole of cellulose. Under the above conditions cellulose conversionis 100%. The catalyst is stable under hydrothermal conditions of the process, it is easily separated from the liquid phase with the external magnetic field and can be reused. Therefore, the results of the research prove the advantages of the use of magnetically retrievable catalysts in biomass processing into chemicals and second-generation biofuel.

This work was funded by the Russian Foundation for Basic Research, the project 15-08-00455.

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Gel synthesis and photo catalytic activity of titanium dioxide with Au and Cu

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Previously it was investigated the influence of silver and gold ions, modifying the anatase surface, as well as calcinations procedure and UV irradiation of Ag-Cu/TiO_2 on its catalytic activity in vapor ethanol decomposition in oxygen free conditions [1,2]. The aim of this study was to synthesize by gel method ultrafine amorphous TiO_2 powders with introduced $CuCl_2$-$AuCl_3$ and to test the Dye methylorange photodecomposition (DPD) before and after Cu,Au/TiO_2 xerogels crystallization. The hydrolysis-condensation reaction between TBT and TEG was proceeding in butanol media with structure evolution of TiO_2 after 120, 450 and 950 °C treatment.

DPD kinetics curves does not correspond the first order, so the initial activity for 1 min irradiation has been chosen as criteria to compare the samples. The rate of photodegradation W_1 that was calculated from plots lnβ–t. The most active was the sample with gold. Copper inhibits Au effect.

The samples were characterized by use of X-ray fluorescence spectroscopy (Clever C-31), AFM-Raman (NTEGRA), DTG/DTA methods and absorption spectra. The ultraviolet light source was broadband lamp PRK-4.

Raman data confirmed only anatase faze in case of calcined samples, but also in case of TiO_2 nanoparticles, in which crystallization occurs after low temperature drying (120 °C). The morphology of smooth TiO_2 films on glass support is drastically changed after DPD in aqueous solutions.

Thus, the gold introduction in pseudo amorphous TiO_2 augments its photocatalytic activity in model reaction of dye degradation. The binary modification $Au_{25}Cu_{75}$ also demonstrates good result.

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The composition, structure and photocatalytic properties of Fe-containing oxide layers on titanium

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One of the most important ecological problems of our time is the treatment of wastewater containing highly toxic and stable organic pollutants, particularly phenolic compounds. Using of heterogeneous photocatalysis allows one to oxidize organic substances with high mineralization at relatively low temperature.

Currently, titanium dioxide is the most studied and effective photocatalyst for decomposition of wide range of organic and inorganic toxic substances. One of perspective direction of efficiency increase of TiO_2 photocatalyst is modification of TiO_2 with transition metal ions, such as ferric species [1-2].

Plasma electrolytic oxidation (PEO) is one of the methods for technological generating multicomponent oxide coatings on metals. PEO is electrochemical oxidation of metal or alloy surface under electric spark and arc discharges [3].

The objective of this work is to prepare PEO-layers on titanium in silicate or phosphate electrolyte with an addition of $K_3[Fe(CN)_6]$ and study their characteristics and photocatalytic activity in phenol degradation.

Oxide coatings were prepared by plasma electrolytic oxidation of titanium in aqueous electrolyte containing Na_2SiO_3 or Na_3PO_4 with addition of various concentration of $K_3[Fe(CN)_6]$.

Phase composition of the formed samples was determined by X-ray diffraction (XRD) analysis. Surface morphology was characterized by scanning electron microscopy (SEM) equipped with energy dispersive X-ray (EDX) spectroscopy and X-ray microprobe analyzer. X-ray electron spectroscopy was used to determine elemental composition of oxide coatings surface. Results

Photocatalytic activity of the coatings was determined by photodegradation of phenol in aqueous solution containing hydrogen peroxide under UV-irradiation. No degradation of phenol occurs without any oxide layers and with coatings formed in silicate or phosphate electrolyte without addition of $K_3[Fe(CN)_6]$. However, when oxide layers are used as photocatalysts, there is a noticeable degradation of phenol increasing with concentration of $K_3[Fe(CN)_6]$ in studied electrolyte.

The phenol degradation degree on Fe-containing oxide layers formed in silicate electrolyte is significantly higher (reaches 80%) than phenol degradation degree on coatings formed in phosphate electrolyte (reaches 55%).

It is believed that prepared composite oxide layers on titanium are perspective as heterogenic Fenton like catalyst which can find an application in water purification.

This work was supported by RFBR Grant (project №14-50-00034)

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Компания ТИРИТ занимается поставкой оборудования более 10 лет. Мы работаем с ведущими мировыми производителями оборудования, спектр которого регулярно расширяется. В настоящее время компания специализируется на химических реакторах и оборудовании для проведения синтезов, также у нас имеется испытательное оборудование и оборудование для исследования физических свойств жидкостей, порошков и поверхностей.

СДЕЛАНО В РОССИИ

Мы предлагаем реакторы и фильтры из нержавеющей стали, сделанные в России по чертежам ТИРИТ.

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Наши технические специалисты выезжают на запуск и обучают пользователей работе со сложным оборудованием. На все поставляемые приборы предоставляется гарантия, мы также осуществляем послегарантийную поддержку. Ремонт оборудования, в случае необходимости, производится в сервисном центре в Москве.

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SECTION 3

RESEARCH METHODS IN CATALYSIS

Improvement of catalytic activity of Ag/SiO_2 catalysts in CO oxidation through optimization of metal-support interaction

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Reaction of low-temperature CO oxidation over Ag/SiO_2 catalysts attracts much attention due to practical and theoretical importance. Practical interest is connected with indoor air purification. Investigation of active sites and mechanism of CO oxidation is important for understanding other processes catalyzed by silver. The Ag/SiO_2 catalysts have wide application not only for CO oxidation [1], such processes as vapor phase alcohol oxidation [2] and dehydrogenation [3], oxidation of alcohols in the liquid phase [4] and deep oxidation of formaldehyde [5]. Metal-support interaction plays crucial role for achievement of high activity in many catalytic systems. However, influence of “silver-silica” interaction on the catalytic perfomance of Ag/SiO_2 catalysts in CO oxidation remains still not clear in spite of numerous investigations. The aim of this work is to investigate the silver states consistently after different pretreatments of catalyst during preparation procedure.

A number of Ag/SiO_2 catalysts (5 and 8 wt. %) were prepared on base of different silica calcined at 500, 550, 700 and 900 ^oC (S_{BET}=40-250 m^2/g) using water solution of $AgNO_3$ and incipient wetness impregnation method. Variation of calcination temperature of silica allows to controlling the concentration of OH-groups, which is evaluated by TPD-H_2O method. Additionally, surface charge of silica was estimated at different pH by means of potentiometric titration. The catalysts prepared were tested in CO oxidation and characterized by TPx methods, UV-visible DRS, TEM, H_2-O_2 titration method and TG-DSC-MS. The silver state on the silica surface was studied after each stage of catalyst preparation: 1) impregnation and drying, 2) oxidative pretreatment at 500 ^oC and 3) reduction at 200 ^oC. Two states of silver nitrate were proposed on the basis of TG-DSC-MS results for the Ag/SiO_2-900 sample. The first of these states is amorphous and decomposes at ~150-350 ^oC with exothermic effect. The second state is crystalline and decomposes at 350-500 ^oC with endothermic effect. Formation of amorphous state was observed mainly for silica calcined at 500 ^oC. The concentration of OH-groups effects on the stabilization and crystallization of silver precursor. Crystallization of silver nitrate occurs mainly on the surface for silica with high concentration of OH-groups. Amorphous layer of salt is formed due to high concentration of SiOAg species. Meanwhile, crystallization of precursor occurs mainly in the solution for supports with low density of OH-groups. In this case small crystallites of salt are deposited on the surface. Existence of two states of silver precursor results in formation of different AgO_x species after oxidative pretreatment of catalysts prepared on base of silica with high and low concentration of OH-groups. Formation of Ag nanoparticles with different structure and dispersion was observed after reduction of oxidized catalysts. It was stated that Ag nanoparticles on the silica surface with low concentration of OH-groups have defective structure and high catalytic activity even at subambient temperature. However, optimal molar ratio OH/Ag (or optimal metal-support interaction) in the prepared catalysts is required for obtaining defective Ag nanoparticles with high dispersion and therefore excellent catalytic perfomance in CO oxidation.

This work was supported by The Tomsk State University Academic D.I. Mendeleev Fund Program in 2016.

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Catalytic properties of Sn-containing porous ordered silica materials in glyoxal disproportionation

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Developing of new methods of biomass processing into valuable organic compounds is one of the urgent problems of modern chemistry. Careful attention is paid to syntheses of bifunctional compounds, in particular, glycolic acid, which is widely used in industries [1]. Recently, a large number of works has been devoted to the heterogeneous process for preparing alpha-hydroxy carbonic acid using porous ordered silicates modified with metal cations (such as tin, titanium, zirconium, and aluminum) [2]. The major advantage of this approach is high selectivity toward the dicarbonyl compounds.

One of the important actual problems is to create stable catalysts, which are resistant to leaching of the active component. Moreover, the adsorption of by-products also can be a reason for the catalyst deactivation. Beta and MFI silicalites are known for their water and thermal resistances as well as the ability to substitute transition metal cations in the crystalline lattice in a tetrahedral oxygen configuration.

The aim of the present study is to investigate the catalytic properties of different tin-containing silica materials in the aqueous-phase glyoxal disproportionation reaction.

Tin-containing silicalites with MFI, Beta, SBA-15 (Sn-MFI[4], Sn-Beta[3], Sn-SBA-15[5]) structures were synthesized according to the procedures described in [3–5]. Structures of samples were confirmed by the XRD, FTIR and low-temperature nitrogen adsorption measurements. In addition, the sample based on amorphous silica (Sn-SiO_2) was prepared by the impregnation method. The Si/Sn molar ratio in all materials prepared was 100:1.

Under static conditions the lowest glycolic acid selectivity was observed for the amorphous Sn-SiO_2 catalyst (78 % compared to 90 % over the porous ordered silica catalysts). The formation of the aldols was detected in the reaction mixture. The reason for formation of the by-products can be associated with the presence of the Bronsted acid sites on the amorphous silica surface together with Lewis acid sites. The selectivities toward glycolic acid were similar for the Sn-MFI, Sn-Beta, Sn-SBA-15 samples, while the conversion depended on the catalyst structure. The conversion over the Sn-MFI and Sn-Beta samples was quite high (99 and 86 %, respectively), while the one for the Sn-SBA-15 sample did not exceed 27 % during 24 h of the reaction run. It can result from the partially microporous amorphous structure of the SBA-15. The Sn-MFI and Sn-Beta catalysts were also chosen to test the catalytic properties under flow conditions.

It was stated that the Sn-MFI catalyst was more stable under flow conditions in comparison with the Sn-Beta catalyst.

This work was supported by The Tomsk State University Academic D.I. Mendeleev Fund Program in 2016.

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Ag/CeO_2 and $Ag/CeO_2/SiO_2$ catalysts for oxidative dehydrogenation of ethanol

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Acetaldehyde is one of the most important large-tonnage chemical. It finds numerous applications as an intermediate in organic synthesis. Production of acetaldehyde from ethanol (bioethanol) is a promising and ecofriendly way, especially in low-tonnage industry. Recently, more publications have been devoted to development and preparation of catalysts for this catalytic process. Metals of IB group (Ag, Au, and Cu) are traditional catalysts for oxidative dehydrogenation of alcohols into corresponding carbonyl compounds. Supported Au catalysts have high activity in this reaction [1,2]. However, the formation of acetic acid as a main liquid by-product requires additional purification of the product. Cu catalysts have low selectivity due to total oxidation of ethanol [3]. Ag-containing catalysts are the most promising catalysts due to high selectivity toward acetaldehyde. The present work is devoted to design of new Ag-containing catalysts supported on CeO_2 and SiO_2 with controllable Ag-CeO_2 and Ag-SiO_2 interfaces for oxidative dehydrogenation of ethanol.

A series of silver catalysts was prepared. The catalysts based on mesoporous silica were synthesized by sequential impregnation, co-impregnation and impregnation of pre-reduced CeO_2/SiO_2 support by aqueous solutions of the corresponding nitrates. The Ag/CeO_2 catalysts with controllable Ag-CeO_2 interface were prepared by impregnation and co-precipitation techniques. The Ag loading was 10 wt.% in all catalysts. Specific surface area (S_{BET}) and pore size distribution of the samples were determined according to the N_2 sorption using TriStar II 3020 analyzer (Micromeritics, USA). XRD patterns were recorded with Shimadzu XRD-6000 diffractometer using CuKα in the range from 10 to 80° (2θ). The structure of the catalysts and distribution of components were studied by TEM using the JEM-2200FS microscope. The reducibility of the catalysts and features of the Ag-SiO_2 and Ag-CeO_2 interactions were studied by TPR-H_2 using ChemiSorb 2750 analyzer (Micromeritics, USA). The catalytic properties of the prepared catalysts in ethanol dehydrogenation were tested in a flow fixed-bed quartz reactor at atmospheric pressure. The reaction mixture containing 2 % vol. of C_2H_5OH and 18 % O_2 in He was passed through the catalysts (0.25-0.5 mm, 0.5 cm^3) with a rate of 60 ml/min. The reactor effluent was analyzed by integrated online GC with a flame-ionization detector to determine ethanol, acetaldehyde, acetic acid and diethyl ether.

It was shown that the order of introduction of silver and ceria influenced on the activity of the $Ag/CeO_2/SiO_2$ catalysts in ethanol dehydrogenation. The sample, prepared by impregnation of pre-reduced CeO_2/SiO_2 support, had higher catalytic activity. This was connected with a strong interfacial interaction of Ag and CeO_2 on the SiO_2 surface. It was also shown that for the Ag/CeO_2 catalyst, prepared by co-precipitation techniques, a strong metal-support interaction was observed, which led to increased catalytic activity. For the Ag/CeO_2 catalysts 15% conversion of ethanol to acetaldehyde was achieved at 85 °C, but the selectivity reduced at temperatures above 150 °C. Generally, for all Ag-containing catalysts acetic acid, diethyl ether and other liquid by-products were not formed, CO_2 was the main by-product.

Thus, the $Ag/CeO_2/SiO_2$ and Ag/CeO_2 catalysts can be considered promising to be used in production of high-purity acetaldehyde from ethanol or bioethanol. The reason for the high activity of these catalysts can be attributed to small Ag and CeO_2 particles and their closed interaction.

This work was supported by "The Tomsk State University Academic D.I. Mendeleev Fund Program" grant in 2015-2016.

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Stability of $Ag_2Cu_2O_3$ catalyst under reaction conditions

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Mixed silver-copper oxide $Ag_2Cu_2O_3$ has a tetragonal crystal structure of a paramelaconite type (ISCD, CC=87609). The structure exhibits the following features: (a) two non-equivalent lattice oxygens; (b) rhomboid distortion of square planar CuO_4 fragments; (c) the non-typical elongated Ag-O bond. The interest to $Ag_2Cu_2O_3$ in heterogeneous catalysis relates to its catalytic properties in low-temperature oxidation of CO [1] and selective alcohol oxidation [2]. However, the paramelaconite structure is known to be metastable [3]. So, it is necessary to investigate the stability of $Ag_2Cu_2O_3$ under reaction conditions.

In this study, mixed oxide $Ag_2Cu_2O_3$ was prepared by co-precipitation in alkaline solution. The combination of XRD, TEM and XPS methods was applied to study structure and surface composition of $Ag_2Cu_2O_3$.

According to XRD the as-prepared sample contained only particles with paramelaconite structure. Such particles with brick-like morphology are elongated along *c* axis. Air storage of $Ag_2Cu_2O_3$ during 4 months resulted in the appearance of metallic silver phase (up to 2 wt.%). However, no any crystallized copper-containing phases were detected in this sample. In accordance with EFTEM data the initial $Ag_2Cu_2O_3$ bricks after long air exposure were covered by round-like silver-containing 10-20 nm particles and thin copper-rich layer. The small thickness of copper-rich layer can be a reason for the absence of any XRD signal for CuO_x structures. Moreover, the exfoliation of copper-rich layers was observed.

Using *in situ* XRD the mixed oxide was studied under different reaction conditions (air, He, CO, $CO+O_2$) during calcination up to 500°C. It was observed that the initial decomposition of $Ag_2Cu_2O_3$ structure at temperature 100-150°C was accompanied by the appearance of Ag^0 traces only. The temperature of full decomposition into Ag^0 and CuO_x was varied in 250-350°C range depending on Red-Ox potential of reaction medium. Prolonged treatment of $Ag_2Cu_2O_3$ by catalytic $CO+O_2$ mixture at 150°C during more than 3 hours resulted in the appearance of metallic silver.

To study the initial stage of $Ag_2Cu_2O_3$ decomposition the prolonged and powerful exposure by electron beam was performed in microscope chamber immediately. Analysis of electron microdiffraction images showed that silver particles were epitaxially grown relatively to the initial $Ag_2Cu_2O_3$ particles. In accordance with *in situ* XRD data the decomposition of $Ag_2Cu_2O_3$ under catalytic conditions was accompanied by the significant decrease of crystal size along *a* and *b* directions only, while no significant change was found for crystal size along *c* axis. The evident growth of *a* lattice parameter was additionally observed.

Using XPS data the Cu/Ag and O/(Cu+Ag) surface ratios were monitored during the calcination of $Ag_2Cu_2O_3$ under UHV conditions. The observed changes were discussed in comparison with *in situ* XRD and TEM results.

Based on all obtained data the overall scheme of $Ag_2Cu_2O_3$ decomposition under reaction conditions is proposed. The possible reasons of $Ag_2Cu_2O_3$ instability during air storage are discussed.

This work was supported by RFBR, research project No. 16-33-00202.

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Study of rhodium, palladium and platinum foils treated in the process of catalytical ammonia oxidation by scanning electron microscopy

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Ammonia oxidation with air on platinum catalyst gauzes is widely used in chemical industry for synthesis of nitric acid [1]. It is well known that during this process the gauzes undergo deep structural rearrangement of surface layers (catalytic etching) leading to the loss of platinum and decrease of catalytic activity [2-3]. To determine the role of individual metals: Pt, Pd and Rh in the catalytic etching of platinum catalyst gauzes during the NH_3 oxidation, we carried out detailed investigation of the surface microstructure of platinum, palladium and rhodium catalysts treated in the reaction medium (NH_3+O_2). Each sample was assembled into a package with four platinum gauzes required to maintain standard conditions of the NH_3 oxidation process. A laboratory flow reactor made of a quartz tube with the inner diameter of 11.2 mm was used at the feed (ca. 10% NH_3 in air) flow rate 880-890 l/h, the gauze temperature 860±5 °C and total pressure about 3.6 bar. The surface microstructure was studied using a scanning electron microscope (SEM) JSM-6460 LV (Jeol).

The SEM study of polycrystalline Pt, Pd and Rh foils after treatment at T~860°C for 5 h in the reaction medium (~10% NH_3 in air) revealed differences in the surface microstructure of these samples. The O_2 reaction with Rh during the catalytic oxidation of NH_3 over rhodium foil results in deep rhodium oxidation followed by the formation of a continuous layer of Rh_2O_3 crystals with the size 1-2 μm. Fast reaction of gaseous NH_3 molecules with O atoms of rhodium oxide leads to the formation of oxygen vacancies and movement of Rh atoms to the surface of the oxide crystals. Rh atoms quickly migrate over the oxide surface and desorb into the gas phase. Increased concentration of Rh atoms in the near-surface gas layer initiates the formation and gradual growth of elongated pyramidal Rh crystals with low concentration of defects. The O_2 interaction with Pd during the NH_3 oxidation on palladium foil leads to intense dissolving of oxygen atoms at defects and in the metal lattice, whereas the resulting oxide PdO quickly decomposes under these conditions. The reaction of gaseous NH_3 molecules with absorbed oxygen atoms O_{abs} with the formation of gaseous NO results in local overheating of the surface initiating the release of metal atoms to the surface. Adsorbed Pd atoms quickly migrate over the metal surface and get incorporated into energetically the most favorable sites. Due to these processes, pits, pores and crystalline facets grow on the surface, whereas grains are gradually reconstructed into faceted crystalline agglomerates with through pores formed due to the growth and merging of pits. So, dramatic structural reconstruction of the foil surface layer (catalytic etching) with the formation of a rough layer takes place during the catalytic NH_3 oxidation with air on Pd. The O_2 interaction with platinum during the NH_3 oxidation over Pt foil results in removal of the surface carbon impurities followed by dissociative chemisorption of oxygen on the surface. It is well known that oxygen dissolution in the Pt lattice with the formation of oxide phases is substantially slower than on Pd and Rh. Small amount of oxygen atoms can be absorbed at the grain boundaries and other defects. The NH_3 reaction with O_{abs} at these defects initiates release of a few Pt atoms to the surface leading to weak etching of the platinum foil surface.

This work was supported by Russian Academy of Sciences and Federal Agency of Scientific Organizations (project 44.1.17).

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Reductive activation of the Ru-promoted Co-Al catalyst: kinetics and mechanism

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We report the experimental study of the effect of ruthenium on the kinetics and mechanism of cobalt-alumina catalyst reduction by means of thermal analysis (TG-DTA) and in-situ synchrotron radiation (SR)-XRD, as well as of the catalytic performance of these Co-Ru/alumina catalysts in the Fischer-Tropsch synthesis.

Cobalt-alumina catalyst (CoAl) was prepared by deposition by precipitation of Co (11.4 wt. %) during urea decomposition method using δ-Al_2O_3. Ruthenium promotion was performed by impregnation with aqueous solutions of $RuNO(NH_3)_2(NO_3)_3$ complex with concentration corresponded to Ru loading of x = 0.2, 0.5 and 1 wt. %. The precursor of the catalysts were calcined in flowing argon at 350 °C.

TG-DTA and XRD data concord that ruthenium promotes both reduction steps $(Co,Al)_3O_4 \rightarrow (Co,Al)O_{1+x}$ and $(Co,Al)O_{1+x} \rightarrow Co^0$ and lowers the reduction temperatures by more than 100 °C. The metallic cobalt phase is distinguished by XRD: at 500 ^oC for Co-Al, at 350 ^oC for Co-Ru(0.2)Al, and at 300 ^oC for Co-Ru(1.0)Al. The model-free kinetic analysis (Ozawa-Flynn-Wall isoconversional method) showed that the activation energy values for the reduction processes accordingly decrease. Analysis of the coherent scattering size of the main cobalt-containing phases (spinel like $(Co,Al)_3O_4$, NaCl-like $(Co,Al)O_{1+x}$ and metallic Co) together with non-linear regression kinetic modelling of the thermal (TG/DTG) curves allowed to elucidate some common features of the reduction mechanism for promoted and non-promoted Co-Al catalysts: (1) formation of multiple nuclei of CoO phase within one crystallite of Co-Al spinel-like oxide and further transformation following Johnson-Mehl-Avrami-Erofeev-Kholmogorov (JMAEK) kinetics, (2) kinetic control of CoO reduction process by the step of the metallic nucleus formation, which is followed by its slow growth, limited by Jander diffusion of oxygen through the Co-Al oxide shell. According to these findings, the ruthenium promoter affects the rate of new phase nuclei formation.

The promoted catalysts can be activated at moderate temperatures, they retain high activity and have beneficial selectivity in the Fischer-Tropsch synthesis.

The work was performed in the framework of the joint Research and Educational Center for Energoefficient Catalysis (Novosibirsk State University, Boreskov Institute of Catalysis) and was supported by Russian Government Decree № V.45.3.6.

Selective aqueous-phase hydrogenation of 2,4,6-trinitrobenzoic acid to cyclohexane-1,3,5-trione trioxime over Pd/Sibunit catalyst

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By using of ^{1}H and ^{13}C NMR spectroscopy, it was established that the catalytic hydrogenation of 2,4,6-trinitrobenzoic acid to 1,3,5-triaminobenzene can proceed via the formation of 1,3,5-*tris*(hydroxyamino)benzene, 3,5-*bis*(hydroxyamino)aniline, 5-(hydroxyamino)-1,3-diaminobenzene and cyclohexane-1,3,5-trione trioxime. As a result of aqueous-phase hydrogenation of sodium salt of 2,4,6-trinitrobenzoic acid in the presence of 5 % Pd/Sibunit catalyst at a temperature of 50 ^{o}C and pressure of 5 bars, a high yield of cyclohexane-1,3,5-trione trioxime (about 70 %) was achieved. Unusual reduction route via the formation of trioxime can be caused by the nature of catalyst, chosen conditions of the reaction as well as nature of substrate (effect of substituent). The selective formation of cyclohexane-1,3,5-trione trioxime allows to consider the catalytic hydrogenation of sodium salt of 2,4,6-trinitrobenzoic acid as a new method for the synthesis of this compound.

Characterization of catalyst and identification of reaction products were performed using equipment of the Omsk Regional Center of Collective Usage. This work was supported by RFBR Grant No. 16-03-00601.

XPS study of active centers of Pt/CeO_2 catalysts for low temperature CO oxidation

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Platinum catalysts supported on metal oxides are among the most used and universal catalysts for a wide spectrum of oxidation reactions. Platinum is often combined with ceria as a catalyst intended for important reactions, in particular, CO oxidation, PROX and WGS. PGM/CeO_2 (PGM – platinum-group metals) systems are prospective catalysts according to its high activity in low-temperature CO oxidation (LTO CO). In this case, investigation of platinum state as an active component in PGM/CeO_2 and metal-support interactions has a great importance for understanding high activity behavior in LTO CO for such systems. X-ray photoelectron spectroscopy (XPS) is a key method for such investigations due to its surface and electronic-state sensitivity.

Coprecipitation from platinum and cerium nitrates was used in this work to synthesize samples with the platinum content of 1, 8 and 20 wt.% under the assumption of anhydrous Pt/CeO_2 samples. Calcination temperature varied from 450°C to 1000°C. Catalytic activity measurements were performed using the temperature-programmed reaction (TPR-$CO+O_2$). It showed that increase in calcination temperature leads to decrease in LTO CO activity for all samples. However, samples with relatively high Pt loading (8 and 20wt.%) calcined at 450°C and 600°C showed abnormal catalytic behavior in LTO CO. The dilution method employed in the case of high-loaded catalysts made it possible to obtain the initial regions of CO conversion curves with low values of conversion (<15%) and to then calculate the activation energies. The calculations yielded the anomalously low value of E_a = 10.5 kJ/mol, which indicates the existence of a concerted mechanism of CO oxidation providing the main contribution to LTO CO.

The state of platinum as an active component was studied using XPS before and after reaction for all samples. The main state of Pt with binding energy $E_b(Pt4f_{7/2})$ = 73.0 eV, which corresponds to solid solution $Pt_xCe_{1-x}O_{2-x}$, was observed for all catalysts. Another Pt4f spectra component with $E_b(Pt4f_{7/2})$ = 71.0 eV responsible for metal particles formation was observed for high temperature calcined samples. It seems interesting that for high-active ones (8 and 20wt.% $T_{calcination}$< 600°C) an additional component with $E_b(Pt4f_{7/2})$ = 74.5 eV was found. This highly oxidized state of Pt formally can be attributed to Pt^{4+}. It should be noted also that for all the samples, irrespective of platinum loading, the Pt4f spectra of the catalysts before and after their catalytic testing did not differ from each other, which means that the reaction medium did not exert a significant effect on the state of active component. Moreover, it was found that after TPR CO oxidized states of Pt haven't vanished. To exclude a reaction with oxygen of ambient air after removing samples from reactor to spectrometer, ex-situ experiments were carried out. The most active catalyst (20%Pt/CeO_2 calcined at 450°C) was treated in spectrometer varying sample temperature in CO and O_2 subsequently to simulate Red-Ox cycles occur in catalytic reaction. According to XPS and TPR $CO+O_2$ testing reaction the presence of Pt^{4+} might be connected with such catalytic activity shown for high Pt-loaded catalysts. This data indicates on the existence of a concerted mechanism of CO oxidation providing the main contribution to LTO CO.

This work was partially supported by the Ministry of Education and Science of the Russian Federation (President's grant for young scientist MK-6911.2016.3).

Dimethoxymethane steam reforming over $CuO-CeO_2$ and CuO-ZnO alumina supported catalysts

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Polymer electrolyte membrane fuel cells (PEMFC) are considered as an alternative environmentally sound source of electric power. Such fuel cells are usually fed by pure hydrogen or hydrogen-rich gas mixtures produced by catalytic conversion of hydrocarbons or oxygenated hydrocarbons.

Dimethoxymethane (DMM), as well as methanol and dimethyl ether, is an easy to synthesize oxygenated compound of C_1 chemistry. DMM is a nontoxic and environmentally benign chemical. It is a liquid under normal conditions, therefore can be easily stored and handled. These facts together suggest that DMM is a promising feedstock for production of hydrogen-rich gas for PEM FC applications.

Steam reforming of DMM is described by equation:

$CH_3OCH_2OCH_3 + 4H_2O = 8H_2 + 3CO_2$

Beside this reaction, a reverse WGSR may proceed to produce carbon monoxide:

$CO_2 + H_2 = CO + H_2O$

DMM SR is similar to steam reforming of dimethyl ester: this process proceeds via a consecutive two-step reaction mechanism: the first step is hydration of DMM to methanol and formaldehyde over acidic catalysts (or acid sites of the catalyst); the second step is steam reforming of the produced methanol/formaldehyde over Cu-based catalysts (or Cu-based sites of the catalyst) to hydrogen-rich gas [1-4].

Based on these scheme and the previous works, $CuO-CeO_2$ and CuO-ZnO alumina supported catalysts could be efficient catalysts for DMM steam reforming.

The present work reports results of kinetic experiments on DMM steam reforming and characterization of catalysts by number of methods, such as TPR, XRD, TEM, EDX, HAADF-STEM, FTIR in situ. To elucidate the role of each catalyst component in DMM SR, the data on the catalytic performance of γ-Al_2O_3, CuO/γ-Al_2O_3, ZnO/γ-Al_2O_3 and CeO_2/γ-Al_2O_3 are presented as well. Based on this data, nature of active sites and mechanism of the reaction are discussed.

It was shown that those catalysts provided complete DMM conversion under atmospheric pressure, T~300 °C, GHSV = 10000 h^{-1} with hydrogen productivity of ~15 L $H_2/h\cdot g_{cat}$ and CO content in hydrogen-rich gas below the equilibrium value (<1 vol.%). The latter fact is important as it allows using a simpler scheme for production of hydrogen-rich gas for PEM FC application that dictates strict requirements regarding the CO impurity.

Based on the data obtained, it was shown that the catalytic performance of $CuO-CeO_2/\gamma-Al_2O_3$ and $CuO-ZnO/\gamma-Al_2O_3$ in DMM SR is associated with the γ-Al_2O_3 acid sites and alumina-supported copper-cerium/zinc oxide species, which are responsible for, respectively, DMM hydration and methanol/formaldehyde SR.

So, bifunctional $CuO-CeO_2/\gamma-Al_2O_3$ and $CuO-ZnO/\gamma-Al_2O_3$ catalysts containing on their surface both acidic and copper-based sites are active and selective for DMM SR to hydrogen-rich gas with low (1 vol.%) CO content.

This work was supported by the RFBR grant 14-03-00457a and by Russian Academy of Sciences and Federal Agency of Scientific Organizations (project V.44.2.9.)

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Activity of Electron-Acceptor Sites during Catalytic Dehydrochlorination over Metal Oxides

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Nanocrystalline oxides, such as MgO, ZnO, TiO_2, γ-Al_2O_3, were shown to be highly efficient and active adsorbents for many toxic chemicals including air pollutants and chemical warfare agents [1]. In this study dehidrochlorination of 1-chlorobutane was chosen as a model reaction for investigation of the sorbents ability for decomposition of halogenated organics.

It was shown earlier that catalytic activity of nanocrystalline MgO in dehydrochlorination substantially increases with time due to the MgO conversion to $MgCl_2$ [2] followed by increase of the acid sites concentration. Moreover, this process coupled with a surface area decrease indicates that more active sites are formed on the surface during this reaction. Acid sites can be characterized using aromatic molecules as a spin probes for EPR spectroscopy [3].

Nanocrystalline and commercial MgO and γ-Al_2O_3 samples were studied. The samples were placed in an EPR sample tube, activated in an argon flow for 1 h at the reaction temperature, and subjected to reaction with 1-chlorobutane. Its conversion to a mixture of butenes was monitored by gas chromatography. After the reaction was carried out for desired time, the sample was quickly cooled down to room temperature and filled with a 2×10^{-2} M solution of perylene or anthracene (spin probes) in toluene. The concentration of electron-acceptor sites was determined by double integration of the EPR signal registered immediately after the spin probe adsorption and after additional heating at 80°C for 18 h.

The catalytic activity of nanocrystalline aerogel-prepared MgO was found to increase significantly during the dehydrochlorination reaction, which is accompanied by modification of the MgO surface and bulk with chloride ions. No electron-acceptor sites were observed on the surface of initial MgO samples. They appeared only during the reaction. Their concentration normalized per unit mass gradually increased during the reaction due to the surface chlorination. A good correlation was observed between the catalytic activity and the concentration of electron-acceptor sites.

For the first time the concentrations of electron-acceptor sites were measured during a catalytic reaction. The concentration of elector-acceptor sites was found to correlate with the catalytic activity. The obtained results indicate that electron-acceptor sites tested using perylene may be the active sites accounting for 1-chlorobutane dehydrochlorination in the active state of the catalysts. It seems to be very important to study possible correlations between the concentrations of electron-acceptor sites and catalytic activity of various catalytic reactions believed to take place on surface acid sites to elucidate the possible role of electron-acceptor sites in these reactions.

This work was supported by RFBR Grants 16-33-00267 mol_a and 15-03-08070-a.

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Catalytic properties of copper molybdates

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Copper molybdates are known as promising materials for different applications, including temperature and pressure sensors, lasers, electrochemistry, etc. However, their catalytic properties are poorly understood. Copper molybdates, primarily $CuMoO_4$, show high catalytic activity in oxidation of soot [1, 2], $(CH_3)_2S_2$ [3], propene and butenes [4], etc. Catalytic properties of $Cu_3Mo_2O_9$ are poorly characterized. The present work is focused on the study of catalytic properties of $CuMoO_4$ and $Cu_3Mo_2O_9$ in CO and soot oxidation.

Monophasic $Cu_3Mo_2O_9$ and $CuMoO_4$ samples were synthesized by co-precipitation and sol-gel methods, respectively. The samples were investigated by X-ray diffraction (XRD) and temperature-programmed reduction in carbon monoxide (CO-TPR). The catalytic soot oxidation was studied by thermogravimetry (TG) and differential scanning calorimetry (DSC) using NETZSCH STA 449C, while CO oxidation was studied by temperature-programmed reaction using ChemiSorb 2750 system (Micromeritics, USA) with mass-spectrometric analysis.

In case of $Cu_3Mo_2O_9$, the CO oxidation was shown to start at 300°C and complete CO conversion occurs at 500 °C. However, notable CO oxidation was observed at temperatures above 450 °C, when $CuMoO_4$ was used. According to the CO-TPR and XRD data, the catalytic activity of the copper molybdates in CO oxidation correlated with the formation of Cu(I)-containing phases, such as $Cu^{II}_{3-x}Cu^{I}_{x}Mo_2O_{9-x/2}$ and $Cu_6Mo_5O_{18}$ in the case of $Cu_3Mo_2O_9$ and $Cu_6Mo_5O_{18}$ and $Cu_4Mo_5O_{17}$ in the case of $CuMoO_4$.

Both $Cu_3Mo_2O_9$ and $CuMoO_4$ was shown to promote the soot oxidation. In contrast to CO oxidation, soot oxidation for both copper molybdates occurs in the same temperature range from 400 to 600 °C and characterized by two peaks of CO_2 evolution accompanied by two exo-effects at 477 and 533 °C. Similarity of catalytic properties of $Cu_3Mo_2O_9$ and $CuMoO_4$ towards soot oxidation indirectly indicates that soot and CO oxidation occurs over different active sites. Mo-containing sites seem to be crucial for soot oxidation.

Thus, the formation of two types of active sites, namely Cu(I)-containing sites responsible for CO oxidation and Mo-containing sites responsible for soot oxidation, were found to form in $Cu_3Mo_2O_9$ and $CuMoO_4$ under reaction condition.

This research was supported by the Tomsk State University Academic D.I. Mendeleev Fund Program in 2015-2016.

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Active centers formation in model Pt/CeO_2 and Pt/Al_2O_3 catalysts prepared by laser ablation

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Catalysts based on platinum and palladium are among the most used systems in oxidizing reactions. For example, a three-way catalysts for the neutralization of exhaust gases contain all the metals platinum triad - Pt, Pd, Rh (PMG). The PMG/Al_2O_3 catalysts are widely used in oil refining, gas-vapor conversion of hydrocarbons, the PROX reaction, the production of gas sensors, CO combustion and etc. Despite the fact that the catalyst systems based on oxides of variable valence (for example CeO_2, TiO_2 and Fe_2O_3) are extensively studied in worldwide, alumina (Al_2O_3) remains classical and most massive support for different catalysts. The high surface area, thermal and chemical stability, a wide range of functional groups on the surface and, importantly, in low cost are the reasons of its popularity. Thus, despite the canonical catalytic systems MPG/Al_2O_3, investigations of possible new approaches to the synthesis of more dispersed, defective or strongly interacting systems using alumina are in high demand.

The search for new approaches to the synthesis of MPG/Al_2O_3 and MPG/CeO_2 catalysts are also highly in demand due to the need to establish the true factors affecting the catalytic activity. One of the most effective methods for the synthesis of complex nanoscale and nanostructured materials is a pulsed laser ablation of bulk targets in a liquid or gas [1]. Control is achieved by varying parameters of the laser pulse (of the wavelength, pulse power and duration), target composition, as well as the characteristics of the reaction medium (the nature of the solvent, and the presence of impurities and precursor composition).

In the present work the interaction of MPG (especially Pt) with different types of supports – Al_2O_3 and CeO_2 was studied to clarify the possibility of new-type active catalytic cites formation. Four sets of catalysts were prepared by laser ablation of MPG and Ce_{met} / Al_{met} targets in water or ethanol. Synthesis of starting nanomaterials was made using main harmonic Nd: YAG laser (1064 nm, 7 ns, 20 Hz, 180 mJ).

All four set ($Pt/CeO_{2(alc)}$, $Pt/Al_2O_{3(alc)}$, $Pt/CeO_{2(H2O)}$, $Pt/Al_2O_{3(H2O)}$) were dried in air followed by calcination at various temperatures ranging from 450 to 800°C. The catalytic properties of the synthesized catalysts were examined in the oxidation of CO with oxygen using a temperature programmed reaction (TPR-CO + O_2). The experiments were carried out in a flow reactor with in-line mass-spectrometric analysis of the gas mixture. All the catalysts before and after the catalytic tests were studied using set of methods: XRD (Bruker D8 Advance), XPS (ES-300 KRATOS) and HR TEM (JEM 2010, JEOL).

For all sets of catalysts the decrease of catalytic activity in CO oxidation at the calcination temperature growth was observed. At the same time samples prepares in alcohol solution were found to be more active comparing to one prepared in water. According to XDR and HR TEM data alcohol-origin samples have rather small platinum particles size. It could be the reason of difference in catalytic activity. The XPS analysis of all four samples sets showed the presence of platinum in metallic state ($E_b(Pt4f_{7/2})$ = 71.1 eV). At the same time for Pt/CeO_2 samples the MPG-oxide interaction after the calcination at 450 and 600C was established by formation of Pt^{2+} in solid solution form ($PtCeO_x$) described by $E_b(Pt4f_{7/2})$ = 73.0 eV.

It could be concluded that in case of CeO_2 support more active in low-temperature CO oxidation samples could be obtained by laser ablation of metal targets. The variation of liquid phase composition effects on the MPG particles size. The smallest Pt particles could be obtained in case of alcohol solution. In case of CeO_2 support at moderate calcination temperature solid solution MPG-CeO_x could be formed.

This work was partially supported by the Russian Foundation of Basic Research, grant # 16-32-50076.

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Ethylene polymerization over titanium-magnesium catalysts: effect of hydrogen on the numbers of active centers and propagation rate constant

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Hydrogen is widely used in industrial processes of polyethylene production with titanium-magnesium catalysts (TMC) as the molecular weight control agent for preparation of different polymer grades. It is known that hydrogen reduce the activity of titanium-magnesium catalysts at ethylene polymerization [1-3]. There are a lot of speculations in literature about the reasons of this effect, but still there isn't generally accepted theory which could explain the deactivating effect of hydrogen at ethylene polymerization. In this work the data on the hydrogen effect on the number of active centers (C_p) and propagation rate constant (k_p) at ethylene polymerization over titanium-magnesium catalysts with different compound and at the variation of polymerization conditions were obtained by the method of polymerization inhibition with radioactive monoxide (^{14}CO).

It was found that the decrease of the activity at hydrogen introduction to the polymerization media is mostly caused by reduction of the determined average k_p value. The number of active centers is weakly depends on hydrogen. Effect of the hydrogen concentration on C_p and k_p values is studied. It was shown the decrease of the polymerization rate with the increase of hydrogen concentration is caused mainly by the decrease of determined k_p value. Only small decrease of the number of active centers is observed at large molar ratios of H_2/C_2H_4 in gas phase. It was found that the hydrogen effect on the activity and C_p and k_p values do not depend on the monomer pressure in the range of 1-4 bar.

Rest upon the data obtained in this work and using literature data about the hydrogen effect at ethylene polymerization on activity, C_P and k_P values for vanadium-magnesium catalysts [4-5] the scheme of active centers transformation in the hydrogen presence at ethylene polymerization on TMC is proposed. The scheme involves the diethylaluminumhydride reversible adsorption on active centers resulting in temporary stop of the propagation reaction and explains the decrease of polymerization rate and determined value k_p in the presents of hydrogen.

This work was supported by Russian Academy of Sciences and Federal Agency of Scientific Organizations (project V.44.2.1).

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Supported MgO-V_2O_5 catalyst for oxidative dehydrogenation of propane: Effect of Mg:V molar ratio on propene selectivity

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Oxidative dehydrogenation (ODH) of light alkanes is an attractive alternative to produce valuable intermediates for polymer, chemical and petrochemical industries. However, low catalyst selectivity towards alkenes remains the primary challenge. Supported vanadia catalysts have been extensively studied in ODH of hydrocarbons. Their high activity is caused by specific character of the surface vanadia species, with the catalytic performances being significantly affected by the formation of V-O-Cr, V-O-Ti, V-O-Mo, and V-O-Mg bonds. Formation of Mg-V-O species or dispersed $Mg_3V_2O_8$ on the support surface is believed to be a reason for high selectivity of VO_x/MgO catalysts. However, only sparse information concerning the alkane ODH over magnesium vanadates supported on alternative supports is reported in literature. For the supported MgO-V_2O_5 catalysts studied [1-3], the correlation of catalytic performances with the catalyst acidity is mainly considered. No data on magnesium vanadates formation on the surface of commonly used supports, their structure and effect on the catalytic properties are reported.

In our recent work [4], the detailed study of the surface V-Mg-O phase formation for the case of MgO-V_2O_5/Al_2O_3 catalyst with the Mg:V molar ratio of 1:2 revealed strong dependence of the phase composition and structure of the catalyst surface on the preparation approach, with the formation of the surface magnesium metavanadate species resulting in improvement of propene selectivity in the propane ODH. The present work considers the effect of Mg:V molar ratio on the surface phase composition and structure as well as catalytic properties of supported MgO-V_2O_5/Al_2O_3 catalysts in propane ODH.

The samples were prepared by a consequent incipient wetness impregnation of γ-Al_2O_3 support with NH_4VO_3 and $Mg(NO_3)_2$ water solutions. The Mg:V molar ratio in the prepared catalysts was 1:1; 1:2; 3:2. For comparison, a V_2O_5/Al_2O_3 sample was also prepared by the incipient wetness impregnation of the support with NH_4VO_3. The prepared samples were characterized by a complex of methods such as XRD, UV-vis DR and Raman spectroscopes, and H_2-TPR. The catalytic properties in propane ODH were tested in a flow catalytic installation with a fixed bed tubular reactor and an online analysis of the products.

For all MgO-V_2O_5/γ-Al_2O_3 samples, the formation of dispersed $Mg_mV_nO_{m+5n/2}$ magnesium vanadates on the support surface is revealed. The composition and structure of magnesium vanadates formed strongly depends on the Mg:V molar ratio in the samples. The primarily formation of magnesium metavanadate species is observed in the case of the sample with Mg:V ratio of 1:2. The sample with Mg:V ratio of 1:1 is characterized by the formation of a mixture of dispersed MgV_2O_6 and magnesium pyrovanadate species, while the sample with Mg:V ratio of 3:2 is characterized by the formation of a mixture of magnesium pyro- and orthovanadate species.

The formation of dispersed magnesium vanadates in the MgO-V_2O_5/Al_2O_3 samples results in improvement of their catalytic properties in terms of alkene selectivity in comparison with those of the V_2O_5/Al_2O_3, with the increase of the Mg:V ratio in a row 1:2, 1:1 and 3:2 resulting in propene selectivity increase. The sample with the Mg:V ratio of 3:2 shows the highest initial propene selectivity among the samples studied, but low stability in the stream.

This work was supported by the Tomsk State University Academic D.I. Mendeleev Fund Program in 2015-2016.

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Kinetics and process modeling of low-temperature steam reforming of light hydrocarbons on Ni-based catalysts

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Associated petroleum gas (APG) is a mixture of light hydrocarbons (CH_4, C_{2+}) produced at oil fields. Typical APG composition is (vol.%) 50-70 CH_4, 5-10 C_2H_6, 5-15 C_{3+}-hydrocarbons (up to octane), 1-10 N_2, 1-10 CO_2. Due to the presence of C_{3+}-fraction, APG causes engine damage and therefore can not be used as a fuel to generate electricity directly at oil fields. APG also has high dew point temperature and can not be transported by conventional gas pipelines.

Low temperature catalytic steam reforming of light hydrocarbons (LTCSR) is a promising method of APG utilization [1]. The process converts C_{3+}-fraction to methane with additives of CO_2 and H_2; received mixture can be used in combustion engines to generate electricity, or it can be transported to gas processing plants by the pipeline system.

The LTCSR process occurs on Ni-based catalysts at temperature range 250-350 °C. The main chemical reactions can be described as follows [2]:

1) $C_nH_{2n+2} + 2nH_2O \rightarrow (3n+1)H_2 + nCO_2$ $(n > 1)$

2) $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$

This work reports our new results on kinetic study of LTCSR of model mixtures of light hydrocarbons (CH_4, $C_3H_8 - C_5H_{12}$), which composition is close to the realistic APG, over the Ni-based catalyst at $T = 200\text{-}350$ °C and atmospheric pressure.

It was shown, that reaction (2) occurs in a quasi-equilibrium mode at $T > 250$ °C and the LTCSR process is limited by the reaction (1). Effective reaction orders with respect to C_3H_8, C_4H_{10}, and C_5H_{12} are close to one; reaction order with respect to steam is slightly negative or close to zero. Concentrations of CH_4, CO_2 and H_2 do not significantly affect on the hydrocarbons conversion. Effective activation energies of propane, butane and pentane steam reforming are close to each other and range from 120 to 150 kJ/mol.

On the basis of the received data the two-stage macrokinetic model was suggested for LTCSR of model methane-propane-butane mixture. It includes steam reforming of propane and butane rate equations, which are first-order with respect to the hydrocarbon. The model also considers the CO_2 methanation reaction as quasi-equilibrium one.

Comparison of the simulated and experimental data for the model methane-propane-butane mixture shows that proposed model describes well the observed dependences and so, can be used for catalytic reactor design.

The work was supported by Project V.44.2.9 and RFBR project 14-03-00457.

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The Application of Probe EPR to the Investigation of Acidic Catalysts Based on Borate-, Phosphate-, Molibdate- and Tungstate-containing Alumina

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Materials based on chemically modified γ-Al_2O_3 have found broad application as catalysts for many chemical processes. The surface acid sites i.e. electron acceptor (Lewis acid sites – **LAS**) or proton donor (Brønsted acid sites – **BAS**) sites of such systems play essential role in the adsorption and catalytic properties of these materials. It has been recently founded that Pt/B_2O_3–Al_2O_3, Pt/ P_2O_5–Al_2O_3, Pt/MoO_3–Al_2O_3 and Pt/WO_3–Al_2O_3 catalysts demonstrate high activity in hydroisomerization process [1], thus it's necessary to determine the influence of modifier anion on the acid properties of the resulting catalysts.

Probe electron paramagnetic resonance (EPR) spectroscopy is practical and express method that may extend the qualitative and quantitative information about the acceptor surface sites and describe the dynamics of adsorbed species. Nitroxide radicals, for example 2,2,6,6-Tetramethyl-piperidin-1-yl-oxyl (**TEMPO**), or aromatic molecules with low ionization potential, such as anthracene, perylene and their derivatives, are widely used for this purpose [2,3].

In current research acidic properties of hydroisomerization catalysts based on anion-modified alumina were investigated by probe EPR.

Synthesis of B_2O_3–Al_2O_3 (**BA**), P_2O_5–Al_2O_3 (**PA**), MoO_3–Al_2O_3 (**MoA**) and WO_3–Al_2O_3 (**WA**) samples containing 10 and 30 wt. % of modifying oxides is presented in [1]. EPR measurements were carried out on Bruker EMXplus X-band (~9.7 GHz) spectrometer at room temperature. After calcination at 500°C each sample were treated with probe solution (5×10^{-4} M TEMPO in *n*-hexane or 5×10^{-2} M antracene or 2×10^{-2} M perylene in toluene) with further spectra registration and processing as described in [4].

The analysis of EPR-spectra observed after addition of TEMPO to BA and WA shows that the signal of 'TEMPO–LAS' complex is substituted to 'TEMPO–BAS' complex with increasing of oxide content. As for MoA and PA there are almost no changes in EPR spectra, represented almost only by 'TEMPO–LAS' complex, from oxide content for both catalytic systems. All results are in good agreement with simulated spectra.

Quantitative determination of radical cations formed from anthracene or perylene after their interaction with BAS of investigated catalysts allowed us reveal an important role of detected BAS in hydroisomerization reaction. In other words catalysts with high concentration of perylene radical cations such as BA and WA demonstrated high yields and selectivity (up to 97 %) of *iso*-heptanes' forming, while PA and MoA having low radical cation concentration shows worse yields and selectivity (less than 6 %). Thereby the developed method may be an useful tool for the catalyst's activity prediction in hydroisomerization reaction. It's preferably to use a set of spin probe to make more reliable results.

The investigation was carried out in Omsk Research Collaboration Centre SB RAS.

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Structure of $Pt_xCe_{1-x}O_{2-\delta}$ solid solutions

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Pt-CeO_2 system is a key component of there-way catalysts for neutralization of exhaust gases. Although these catalysts have been widely studied, the nature of Pt active center is still debated. According to recent literature publications ionic form of Pt on the surface of ceria plays important role in many oxidation reactions [1]. Many researchers point out that catalytic activity enhance when Pt-CeO_2 solid solution is formed. The solid solution is characterized by homogeneous distribution of Pt ions within CeO_2 structure. According to our latest data increase in Pt loading up to 20 weight % in solid solution dramatically increases catalytic activity in CO oxidation [2]. 90% CO conversion at 0^oC was detected for 20%Pt-CeO_2 sample. However, the structure of Pt-CeO_2 solid solutions has not been studied yet. Therefore the aim of this work is detailed analysis of structure of Pt-CeO_2 solid solution with different Pt loading.

Five series of catalysts with platinum loading of 1, 8, 15, 20 and 30%wt were prepared by co-precipitation method. This method allows obtaining samples with a wide range of Pt content in a solid solution. Samples were synthesized from solutions of platinum and cerium nitrate, followed by calcination at various temperatures ranging from 450 to 1000°C. All samples were studied using set of methods: XRD, XPS and HRTEM. The local structure of Pt-CeO_2 solid solution was analyzed by Pair Distribution function (PDF) method. The diffraction data for the PDF were obtained using synchrotron radiation at station ID21 of the ESRF. λ=0.177Å.

The XRD data indicate that samples with different platinum content and the calcination temperature below 800°C are single-phase. All the peaks were attributed to an oxide with fluorite structure. Metallic Pt or its oxides were not detected. The increase of the calcination temperature above 600°C leads to the formation of metallic Pt. XRD data are fully confirmed by HRTEM, which revealed that the initial samples do not contain any extended platinum species. However, according to EDX microanalysis data platinum is distributed uniformly within entire ceria particles. The lattice parameter of the fluorite phase increases with increase of Pt loading. The fluorite particle size decreases when Pt loading increases. Doping with Pt strongly hinders the sintering of ceria at high temperatures.

According to XPS data the main platinum state in all samples is Pt^{2+}. It can be attributed to platinum in $Pt_xCe_{1-x}O_{2-\delta}$ solid solution. Pt4f spectrum for 1%Pt/CeO_2 samples indicated only single Pt^{2+} state, while for other samples there are two states: Pt^{2+} and additional Pt^{4+}states.

According to PDF data Pt-CeO_2 solid solutions exhibit the main features of a fluorite structure on the local level. In addition to the main fluorite-type distances some additional peaks were detected. These distances can be attributed neither to metallic Pt, nor to platinum oxides. By analogy to Pd-CeO_2 solid solutions that we have studied previously [3], we attribute these additional PDF peaks to Pt-O and Pt-Ce distances in a $Pt_xCe_{1-x}O_{2-\delta}$ solid solution.

This work was supported by the project of Basic budget financing №V.44.1.16 (the SB RAS program V.44.1).

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Silica-supported Fe-Mo-O catalysts for propylene glycol oxidation

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Current trends in the field of "green chemistry" are associated with a search for alternative catalysts based on noble metals (Ag, Au, Pt). Mixed iron and molybdenum oxides are known to show high catalytic activity in various processes. For example, for many years the Fe-Mo-O catalysts have been used in industry to produce formaldehyde through methanol oxidation [1, 2]. The usage of the $FePO_4$ with small additions of Mo as catalysts for oxidation of propylene glycol into valuable organic compounds was presented by M. Ai et al. [3]. The addition of Mo increased the selectivity towards methylglyoxal as compared with the results for FePO4. The main attention was paid to the bulk Fe-Mo-O catalysts. The active component distribution on the support surface increased the activity of the catalysts in propylene oxidation to methylglyoxal.

The aim of the present work is to synthesize the supported Fe-Mo-O/SiO_2 catalysts with different Mo/Fe ratio and study the influence of the phase composition on the catalytic properties of the systems in the propylene glycol oxidation to methylglyoxal.

The Fe-Mo-O/SiO_2 catalysts were synthesized by varying the Mo/Fe molar ratio from 0.5 to 3 (the Mo content in all samples was 10 wt. %). $(NH_4)_6Mo_7O_{24}$ and $Fe(NO_3)_3$ were used as Mo and Fe precursors. $Fe_2(MoO_4)_3$ was prepared as a reference sample by the procedure described in [4]. The supported samples were prepared by incipient wetness impregnation of silica (KSKG, LLC "Salavat Catalyst Plant", with surface area of 345 m2/g) with hot citrate solution containing ammonium paramolybdate and ferric nitrate. The resulting samples were dried at 120 °C and calcined in air flow at 600 °C.

The phase composition of the samples was investigated by the XRD method, the reactivity of the catalysts was described by the TPR-H_2. The catalytic properties of the Fe-Mo-O/SiO_2 catalysts were studied in the gas-phase propylene glycol oxidation to methylglyoxal in the temperature range of 250-500 °C and using different contact times (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, acetaldehyde, acrylic acid, etc.

The influence of the Mo/Fe ratio and phase composition on the catalytic properties of the produced catalysts was revealed. The distribution of the active component on the SiO_2 surface increased the selectivity towards methylglyoxal almost 3 times to up to 14%, compared with the values for the bulk $Fe_2(MoO_4)_3$ sample. The influence of the phase composition in supported catalysts on the final reaction product ratio was studied.

This work was supported by the State University Academic D.I. Mendeleev Fund Program in 2016.

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Oxidative carbonylation of methanol over Cu^+ oxides

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Oxidative carbonylation of methanol is an attractive route for dimethyl carbonate (DMC) synthesis. Methanol, oxygen and carbon monoxide are cheaper comparing to methyl nitrite or ethylene carbonate, which are used for production of dimethyl carbonate now. The reaction of oxidative carbonylation of methanol

$$2CH_3OH + CO + ½\ O_2 = (CH_3O)_2CO + H_2O \qquad (I)$$

is thermodynamically favorable even at room temperature with ΔrG°298= – 227.1 kJ/mol, unlike direct carboxylation of methanol,

$$2CH_3OH + CO_2 = (CH_3O)_2CO + H2O \qquad (II)$$

which is thermodynamically restricted process (ΔrG°298 = 28.5 kJ/mol). Several groups of researchers have reported formation of DMC from CO and oxygen over Cu^+-containing oxide catalysts, like Cu^+-substituted CuY [1] or Cu-ZSM-5 [2]. Low content of Cu^+ cations restricts catalytic activity of these oxides. Higher concentration of Cu^+ cations can be found in $CuMe^{3+}O_2$ (Me=Al, Cr or Co) oxides with delafossite-like structure.

We have synthesized a series of delafossite-like oxides, incl. $CuAlO_2$ and $CuCoO_2$ delafossite, and recorded their FT-IR spectra during consecutive exposition to CO, O_2 and methanol and to methanol, oxygen and CO at elevated temperature, as well as performed the catalytic tests in oxidative carbonylation of methanol. If CO adsorption is followed by oxygen treatment and then methanol is fed over the surface of Cu-Al delafossite, then bidentate and unidentate methoxy-groups are the main surface species at low temperatures. Increasing the temperature leads to oxydation of methoxy to formate and carbonate groups. The catalyst surface becomes reduced and methanol is oxidized via formates to carbon dioxide. If methanol is fed first, then it is replaced by oxygen and CO adsorption comes the last, then the oxydation of methoxy species leads to carbonates and monomethylcarbonate groups. The latter are considered as the intermediates on the route from methanol to DMC [3]. However further treatment of the surface with CO removes methoxy- and methylcarbonate groups and CO_2 and water are produced. These findings are in the agreement with the results of the catalytic tests.

Thus, our experimental data evidence that interaction of CO, oxygen and methanol over Cu^+-containing oxides occurs via carbonate intermediates to carbon dioxide. It means that Cu^+-containing oxides are active in both reactions (I) and (II), however the yield of DMC is determined by the equilibrium of the least favorable process (II) and requires elevated pressure.

The work was performed with the support of the Ministry of Education and Science of the Russian Federation (project no. 221-2014/139).

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TPR and XPS study of Rh/CeO_2 catalysts of low-temperature CO oxidation

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Rhodium is an active component of many catalytic systems showing activity in both oxidation and reduction processes. In particular, Rh/CeO_2 catalysts proved to be active for ethanol and methane steam reforming, methanol combustion, oxidation of CO etc. The interaction of rhodium species with CeO_2 was established to play a crucial role in catalytic activity of the materials, however many aspects of functioning of these systems are still need to be clarified.

The 5.5 wt%Rh/CeO_2 catalysts were synthesized by coprecipitation of Rh and Ce nitrates with subsequent calcination in air at temperatures up to 1000 °C. Their catalytic and physical-chemical properties were studied depending on the calcination temperature. To analyze the nature of active catalytic species the combination of X-ray photoelectron spectroscopy (XPS) and temperature-programmed reactions (TPR -CO+O_2 and TPR-CO) experiments were performed.

Rh/CeO_2 catalysts calcined at 450 °C and 600 °C showed activity in CO oxidation reaction at room temperature with temperature of 50% CO conversion (T50) being about 50°C-60°C. For samples calcined at 800 °C, 900 °C the curves of CO conversion shifted to higher temperatures, while Rh/CeO_2-1000 °C catalyst did not reveal any activity at low-temperatures. The TPR CO experiments show presence of several types of surface and bulk active species in Rh/CeOx system. The catalysts calcined at 450 °C and 600 °C are characterized by high oxygen mobility and reactivity at lower temperature range, while well-crystallized samples active only at T >250 °C.

The XPS data showed the Rh enrichment of surface with increase of calcination temperature due to the segregation of active component. The Rh3d spectra of the initial samples were characterized by main component at binding energy $E_b(Rh3d_{5/2})$ = 309.0-309.2 eV, typical for Rh^{3+} species in Rh-CeO_x solid solution. The small peak at 307.5 eV related to rhodium clusters $Rh_n^{\delta+}$ was also present in Rh3d spectrum of Rh/CeO_2-450 °C sample. No signals corresponded to bulk Rh^0 or Rh_2O_3 species were observed. XRD and TEM data confirmed the XPS results. No reflexes apart from the ones corresponding to the CeO_2 fluorite structure were observed in XRD patterns of samples up to the calcination temperature 1000 °C. TEM images showed only ceria crystallites for the samples calcined at 450 °C and 600 °C. No Rh^0 or Rh_2O_3 particles were detected. However, EDX mapping of the samples area demonstrated that rhodium was uniformly distributed over the entire area.

Analysis of XPS and TPR CO results showed that for samples calcined at lower temperatures, the reduction/reoxidation $Rh_n^{\delta+}\leftrightarrow Rh^{3+}$ proceeds easily due to the high oxygen mobility on the surface as well as in the entire volume of the samples. Opposite to Rh/CeO_2-450 °C and Rh/CeO_2-600 °C samples the reduction/reoxidation process for well-crystallized Rh/CeO_2-900 °C and Rh/CeO_2-1000 °C samples is not so effective leading to substantial decrease of catalytic activity.

The maximum activity in LTO CO demonstrated Rh/CeO_2 catalysts with defective amorphous structure of Rh-CeO_x solid solution phase, characterized by high oxygen mobility that provided effective interaction with CO and facilitated the reoxidation process. Samples remain active up to the calcination temperature 800 °C, above which the crystallization of the system takes place with decrease of oxygen mobility and LTO activity.

This work was partially supported by the Ministry of Education and Science of the Russian Federation (President's grant for young scientist MK-6911.2016.3).

Ag-CeO_2/SiO_2 catalysts with specified component distribution for low-temperature VOCs oxidation

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Volatile organic compounds (VOCs) make a large contribution to the environmental pollution. This requires the development of effective methods to prevent emissions of these substances into the atmosphere. Catalytic deep oxidation of VOCs to CO_2 and water is one of the perspective directions. At the present time, many catalysts are known and can be used for this purpose [1]. Silver supported on different supports (such as: silica (SBA, MCM), oxides of cerium, cobalt, manganese, molybdenum, etc.) is one of promising catalysts [2]. These catalysts have a number of advantages and disadvantages. Thus, Ag/SiO_2 has a high specific surface area and activity in low-temperature CO oxidation [3]. Ag/CeO_2 has high catalytic activity and low specific surface area, low thermal stability and high price.

One of the possible methods to solve these problems consists in supporting of the Ag/CeO_2 catalyst composition on the surface of primarily inert support, i.e. silica [4]. This method allows obtaining the granular catalyst, which combines high specific surface area, thermal and mechanical stability of silica with high activity in VOC oxidation due to the presence of interaction between supported silver and CeO_2 [5]. The aim of this work is to study influence of conditions to support silver and CeO_2 on the silica surface on them distribution and the catalytic properties of the catalyst in oxidation of VOCs.

Series of Ag-CeO_2/SiO_2 catalysts were prepared by wetness impregnation techniques, characterized by N2 sorption, XRD, TPR and tested in low-temperature CO oxidation.

It was shown that the use of citric acid as a stabilizing additive at the stage of deposition led to the formation of small CeO_2 particles (2-4 nm) on the silica surface. The synthesis without citric acid led to nonuniform distribution of CeO_2 on the silica surface. Similar results were obtained for the CeO_2-ZrO_2/SiO_2 catalysts.

It was shown that the obtained Ag-containing catalysts had high activity in low-temperature CO oxidation. The component input order and pretreatment conditions also influenced on the distribution of Ag and CeO_2 on the surface of silica and catalytic properties of the Ag-CeO_2/SiO_2 catalysts in CO oxidation. Catalytic properties of the prepared catalysts will be tested in deep oxidation of formaldehyde.

This work is supported by the RFBR (grant 16-33-50132 mol_nr).

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Influence of heat treatment conditions for Cr-Al catalyst of the tetrachloroethylene hydrofluorination into pentafluoroethane

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Activity and selectivity of the catalyst which used for pentafluoroethane $CHF_2–CF_3$ (R-125) synthesis by gas-phase hydrofluorination of perchloroethylene $CCl_2=CCl_2$ depends on initial content of main catalytic components – chromium oxides and promoting and stabilizing admixture Al, Mg, Ni, Zn and parameters of pretreatment [1-3]. Pretreatment of Cr-containing catalysts includes heat treatment and hydrofluorination.

In this work we studied the influence of the temperature and gas phase composition of heat treatment on the physicochemical and catalytic properties of high-concentrated chromium-aluminum catalysts.

Precursor of Cr-Al catalysts containing 95 wt % chromium oxide Cr_2O_3 and 5 wt % Al_2O_3 were prepared by the addition of a mixture of $CrCl_3$ and $AlCl_3$ solutions to a solution of ammonia (9%) at a constant pH and a temperature of 75–80°C. After the completion of precipitation, the suspension was aged for 1 h at the same pH and temperature values, washed with distilled water, filtered and dried in air at 110–120°C for 12 h. The resulting air-dry sample was then heat-treated between 165 and 600°C using different procedures: treatment in nitrogen or in air.

Thermal analysis (TA) was carried out using a NETZSCH STA-449-Jupiter. Samples were heated from room temperature to 600°C at a constant rate in nitrogen or air flow. The samples were characterized by differential thermal (DTA), thermogravimetric (TG) and differential thermogravimetric (DTG) analyses.

Samples (precursors) after heat treatment were characterized by the specific surface area (BET). It was found that during the heat treatment in nitrogen with a temperature increase from 100 to 500°C samples have lose water, accompanied by an increase of the specific surface from 150 to 300 m2/g. Upon further heating occurs exothermic crystallization to form α-chromium oxide, resulting in reduced specific surface area to 100 m^2/g or less. When the precursor to heat treatment in air as sample loss of water is observed, but the larger specific surface area is not observe. At temperatures above 200°C is observed oxidation Cr (III) to Cr (IV) and with further heating above 400°C result in loses oxygen by CrO_2, becoming Cr_2O_3, crystallization and reduction of its specific surface area to 50 m2/g. This can be explained taking place in an oxidizing environment according to the following process chart showing the transition from amorphous (am.) chromium to crystal (cr.) state:

$$Cr_2O_3(\text{am.}) \xrightarrow{200–370^0C} CrO_2(\text{am.}) \xleftrightarrow{370\text{-}400^0C} Cr_2O_3(\text{am.}) \xrightarrow{410–420^0C} \alpha\text{-}CrO_2(\text{cr.})$$

Activity of prepared catalysts was tested in the lab-scale reactor with a fixed bed (volume 2 cm3) in the synthesis of pentafluoroethane (HFC-125) by perchlorethylene hydrofluorination in temperature range 320-360°C and at a pressure of 4 atm.

The influence of heat treatment conditions was studied of high-concentrated chromium-aluminum catalysts. It is found that heat treatment of the catalyst in an oxidative atmosphere (air) at temperature about 450°C can increase catalyst activity at about 45% compared with traditional method of heat treatment in inert atmosphere (nitrogen).

This work was supported by the Russian Foundation for Basic Research, project No. 15-08-04789-a.

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Thesis title Formation of nickel catalysts surface for hydrogenation reactions with desired adsorption properties

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The main question of the catalysis science is the prediction of catalytic activities. A promising area of searches can be regarded as the use of the achievements of the adsorption theory for the synthesis of the catalyst surface with desired adsorption properties in relation to the reactants. The surface of hydrogenation catalysts based on transition metals can be formed and be modified with its properties directly during synthesis, in different operating conditions, and while introduction of various compounds with high adsorption properties, examples of such compounds are catalyst poisons. The purpose of this study was to determine the correlation such as "catalytic activity - surface structure - adsorptive properties" of catalysts for hydrogenation reactions of "carbon-carbon" multiple bonds at a variety of process conditions.

We used such catalysts as skeletal nickel catalysts (Raney's nickel) and nickel inflicted on a different support (silica, alumina, carbon). In the work the methods of supported nickel catalysts synthesis was developed to allow controlling the concentration of metal on the support surface, and the value of active metal surface area.

The catalytic activity was tested in a liquid phase (0,1 ÷ 0,9 MPa 30 °C) and gas phase (0.1 MPa, 150 °C) hydrogenation of maleic acid diethyl esther. In order to control the adsorption capacity of the catalyst in relation to the reactants, especially to hydrogen, sulfur compounds were introduced into the reaction system. The variation of the synthesis methods, conditions of catalytic process and introduction of catalytic poison deliberately allowed to adjust the surface properties of nickel and to receive catalysts with the specified parameters of activity and selectivity. The composition and the properties of the catalysts surface were studied using XRD, the low-temperature adsorption, the laser dispersion analysis, the atomic absorption, the infrared spectra, and the adsorption calorimetry. Adsorptive properties of the produced catalysts were studied using a set of thermal analysis and mass spectrometry, comprising: a synchronous thermal analysis instrument STA 449 F3 Jupiter® NETZSCH and mass spectrometer QMS 403 C Aeolos®, reaction gas dispensing system PulseTA®, vacuum system, and high-temperature furnace and a sensor for the STA 449 F3 Jupiter®.

The experimental data obtained in the work allowed to search for correlations structure vs. composition of the nickel catalysts surface vs. their activity for the reduction reaction of the double bond "carbon-carbon". It was proved by direct experimental method the existence of various forms of adsorbed hydrogen on the surface, and was determined thermochemical characteristics of these forms. Approaches to creating optimal nickel surface for reduction reaction of the individual classes of organic compounds were showed.

The practical part of the work is carried out as part government task (project 1800). The theoretical part of the work is supported by the Ministry of Education and Science (project №4.1385.2014/K).

A Kinetics Study of Homogeneous Catalytic Reaction of Aldol Condensation of Acetone and Formaldehyde

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The products of aldol condensation of acetone with various aldehydes, for instance formaldehyde, have very high industrial demand. These materials are used mainly as composite binders in construction and mending of oil wells as well as modifying agents for glues and other polymer systems [1,2]. It is possible to obtain different products possessing a controlled selection of useful parameters depending on synthetic conditions, which is very convenient for preparation of materials with the desired properties involving the same reagents. It should be noted that such versatility can cause technological problems due to the lack of determined regularities of the process and proper study of reaction kinetics in various conditions. The preliminary experiments have shown that the kinetics of aldol condensation of acetone and formaldehyde is influenced the most by temperature and concentration of alkaline catalyst, while the properties of final products (oligomers) depend more on the reactant ratio. In this work the kinetics of acetone and formaldehyde consumption and formation of intermediate products of their condensation products in alkaline conditions is studied, as well as the influence of temperature on the kinetics of this process with fixed component concentrations in the starting mixture in isothermal conditions.

The experiments were carried out with the use of calorimeter «ATLAS» (Syrris) in the mode of heat compensation method with automatically controlled pH, temperature of reaction mixture and reaction enthalpy. The reaction temperature was varied in the range of 25 ÷ 55 °C with constant starting concentrations of acetone and formaldehyde in the presence of alkali metal carbonates used as catalyst. Formaldehyde was used as 37% wt. water solution stabilized by methanol. Acetone (analytical grade), sodium and potassium carbonates were used without additional treatment. The forming mixture of oligomers was analyzed via gas chromatography and high efficiency liquid chromatography with mass spectrometer. The identification of by-products and oligomers was carried out via TOF mass-spectrometer with electrospray ionization as well as NMA, FTIR and Raman spectroscopy. The resins obtained after concentrating the solutions of oligomers, as well as their polymerization products, were studied via synchronized TG-DTA/DSC method.

According to the analysis of the kinetic curves, it was shown that formaldehyde reacts with acetone with molar ratio ~ 3:1, which is preserved regardless of reaction temperature. The detailed study of TOF mass spectra of reaction mass allows concluding that the structure of main oligomers includes the basic fragment of diacetone alcohol (DAA) which is characteristic for acetone autocondensation on the beginning stage of oligomer formation. Next, an interaction between formaldehyde molecules and DAA occurs, resulting in the formation of respective methylol derivatives. Chromatographic data indicates on equilibrium formation of DAA. The products of direct condensation of acetone and formaldehyde are also detected in reaction mixture. According to the analysis of obtained data, a reaction mechanism is suggested, by-products and final products are identified, and the rate constants of main reactions are determined.

This work was supported by “The Tomsk State University Academic D. I. Mendeleev Fund Program” grant in 2016 (8.2.07.2015).

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Effect of Mo:Al ratio in zeolite containing catalysts on their activity in the course of non-oxidative methane conversion

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The process for converting methane to aromatic hydrocarbons under non-oxidizing conditions is of considerable interest as a promising method of natural and associated petroleum gases recovery. Effective catalysts for this process are high-silica ZSM-5 zeolites modified with transition metal ions. Bifunctional properties of these catalysts are due to both acid sites of the zeolite itself and Mo-containing sites [1, 2].

The aim of this work is to study the effect of the Mo:Al ratio in the catalyst systems prepared using zeolites with different silica module (M = 16-80) and the nanoscale Mo powder (NSP) on their activity and stability in the course of non-oxidative conversion of methane into aromatic hydrocarbons.

Mo/ZSM-5 catalysts were prepared via solid-phase synthesis by mechanically mixing the H-form zeolites with a nanosized molybdenum powder. The resulting mixture was calcined at 540 °C for 4 hours. The catalytic activity of the samples was investigated in a laboratory flow setup at 750 °C and the feed space velocity of methane 1000 h^{-1}. The reaction products were analyzed by gas chromatography.

Our previous investigations on the process of methane conversion over Mo-containing zeolites with silica modulus 40 showed that the highest activity and stability were exhibited by the catalyst containing 4.0% Mo nanopowder with the Mo:Al ratio being equal to 1:2. It was therefore of interest to investigate the influence of Mo:Al ratio in the catalysts prepared using zeolites with different silica moduli to achieve the Mo:Al ratio 1:2. For comparison, we prepared zeolite catalysts containing 4.0% Mo NSP regardless of the value of silica modulus.

The tests of catalysts containing 4.0% Mo showed that the lowest activity in the course of methane conversion was exhibited by Mo-containing zeolites with silica moduli 16 and 80. The modified zeolite with M = 30 is characterized by the highest activity in the first 100 minutes of operation, but with the operation time increasing to 380 min its activity is significantly reduced, so it does not exceed 3.1% at the end of the reaction cycle. The highest stability during the whole reaction cycle was exhibited by the sample with M = 40.

The tests for Mo-containing zeolites whose Mo:Al ratio was 1:2 have shown that it was the large amount of Mo nanopowder (8.6%) required to achieve this ratio (Mo:Al = 1:2) in the zeolite with a low silica modulus (M = 16) which resulted in a sharp drop in its catalytic activity and stability. The catalysts with the silica moduli 30 and 40 exhibited close values of methane conversion during the first 140 minutes and then the activity of catalyst with M = 40 began to decline more rapidly than that of the sample with M = 30. Thus, within the subsequent 240 minutes of reaction, the methane conversion over zeolite with M = 40 decreased by 4.7%, while that over the sample with M = 30 by only 2.4%. With the silicate zeolite modulus increasing to 60 or 80 the activity and stability of Mo-containing catalysts in the course of methane conversion are lower as compared with the catalysts prepared on basis of zeolites with the silica moduli 30 and 40.

A comparison of the catalytic activity and stability of a number of catalysts having the Mo:Al= 1: 2 ratio with those having 4.0% Mo has shown that the zeolite with M = 30 is very active in the first 100 minutes of reaction and an increase in Mo content from 4.0 to 4.8% has resulted in a significant increase in the stability of a catalyst with M = 30 after 220 minutes of the reaction.

Thus, the results obtained suggest that the Mo:Al ratio in Mo-containing zeolite systems is of great importance for the formation of active sites of a methane molecule activation and hence for manufacturing the most selective and stable catalysts for the process of methane dehydroaromatization.

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Aluminum derivative peroxides in catalytic system $(t\text{-BuO})_3Al$ – 2t-BuOOH as source of electron-excited dioxygen, $O_2\left({}^1\Sigma_g^+\right)$: a quantum chemical study on a model

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Based on the presented quantum chemical study of the MeOOH/$(MeO)_3Al$ model system, one can conclude that the excited dioxygen, $O_2(b^1\Sigma_g^+)$, is produced in the liquid phase in the catalytic decomposition of *t*-BuOOH. Thus, it was exhibited for the first time that O_2 is generated chemically excited. $O_2(b^1\Sigma_g^+)$ is formed as a result of the successive reactions of aluminum *tert*-butoxide with *tert*-butyl hydroperoxide at the mole ratio of 1:2. In the first step, the aluminum-containing peroxide $(t\text{-BuO})_2AlOOt\text{-Bu}$ for the experimental system or $(MeO)_2AlOOMe$ for the model system is produced. The latter one reacts with the second MeOOH molecule both through the pathway of the substitution of the methoxy group (main reaction pathway) and through the six-membered transition state (minor pathway) with the formation of metastable metal-containing mono–η^2–and bis–η^2–methyl peroxides and the elimination of the MeOH molecule. The formation of the isomeric ozonides $(MeO)_2AlO_3Me$ is the rate-determining step. For the main reaction pathway, the activation energy (E_a) of the intermolecular O atom transfer was calculated to be 159.2 kJ/mol. From ozonide-1,3, $(MeO)_2AlOOOMe$, the corresponding metal dioxygen intermediate, η^1-$(MeO)_3Al{\bullet}O_2$, is generated in the decomposition reaction which ends with the elimination of dioxygen in the electron-excited state, $O_2({}^1\Sigma_g)$. The electronic state of O_2 was established by the analysis of the energy diagram calculated for the $(MeO)_3Al/O_2$ system at the CCSD(T,fc)/cc-pVTZ, CCSDT(Q)/cc-pVTZ, and CAS(14,10)/6-311G(d) theory levels. For the decomposition of η^1-$(MeO)_3Al{\bullet}O_2$, a non-adiabatic pathway, that includes the singlet-triplet transition and leads to the generation of chemically activated ${}^3O_2$, was exhibited.

The conducted simulation makes it possible to propose that the catalytic decomposition of t-BuOOH leads to a complicated oxidizing system being the source of the reactive oxygen species: mono–η^2–, bis–η^2–peroxides, isomeric ozonides, η^1-peroxide, chemically activated (${}^3O_2{}^*$) and chemically excited ($O_2(b^1\Sigma_g^+)$ and $O_2({}^1\Delta_g)$) dioxygen. $O_2({}^1\Delta_g)$ is the product of the decay of the higher excited state. $O_2(b^1\Sigma_g^+)$ is characterized by the significantly shorter lifetime than $O_2({}^1\Delta_g)$. The latter is the product of the spin-allowed transition decomposition of $O_2(b^1\Sigma_g^+)$. One can believe that quenching through the e-v mechanism for $O_2(b^1\Sigma_g^+)$ can create a pathway to exhibit an uncommon reactivity of $O_2({}^1\Delta_g)$ which results from the chemical activation of the substrate by energy excess released in the $O_2({}^1\Delta_g) \leftarrow O_2(b^1\Sigma_g^+)$ relaxation. The formation of the $(t\text{-BuO})_3Al{\bullet}O_2$ complex analogous to $(MeO)_3Al{\bullet}O_2$ predicted here on the basis of quantum chemical study can determine the reactivity of chemically immobilized $O_2(b^1\Sigma_g^+)$. Both pathways make the new chemistry of ${}^1O_2$ possible, that is, the oxidizing activity results directly or indirectly from the reactivity of $O_2(b^1\Sigma_g^+)$. Thus, it may determine important enhancement to famous Fenton and Haber-Weiss chemistry.

A.I. Petrov is thankful to SFU Super - computer Centre (http:cluster.sfu-kras.ru) for generous donation of computer time. O.B. Gadzhiev is thankful for the partial support of this study provided by a grant under agreement of N.I. Lobachevsky State University of Nizhny Novgorod and the Ministry of Education and Science of the Russian Federation.

Chemically modified surface of supported Pt nanocatalysts: a quantum chemical study on selected model clusters

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Methodologies for preparation of facet-controlled nanoparticles (NPs) are developed intensively since the shape-selected nanoparicles exhibit often selective catalytic properties. Moreover, due to shape selection, the NPs can be building blocks of advanced nanomaterials with high surface area, which is an important property for the catalyst. Specific field for these materials is also spintronics and plasmonics. The most methodologies are based on surfactant specific stabilization of the facet. That is, the manipulation of surface energy of a given facet by using surface-binding molecules has been the major synthetic strategy. However, the data on specific adsorption energy are very scarce. In the present, I addressed to these properties.

In order to elucidate catalytic properties of Pt NPs capped by DDT (1-dodecanethiol) in the crotonaldehyde hydrogenation, the presented quantum chemical study of (finite, free) clusters was conducted on Pt_{30}\{111\} (two-layer cluster), Pt_{41}\{100\} and Pt_{40}\{111\} (three-layer clusters) as models for different facets of Pt NPs corresponding to crystallographic planes. The data on Pt_{25}\{100\} were reported earlier [1]. BuSH was used as a model for DDT. Other adsorbates were H_2, syn-and anty-(2*E*)-but-2-enal (crotonaldehyde), propenal (acrolein). In coincidence with the earlier study [1], the reported results were obtained with the BLYP exchange-correlation GGA density functional in conjunction with CRENBS effective core potential (ECP) and orbital basis set for platinum, LANL2DZdp ECP and orbital basis set for sulfur, and 6-31G(d,p) all-electron basis set for carbon, oxygen, and hydrogen atoms.

As was calculated with the BLYP density functional, 1) the exothermicity of the dissociative adsorption is reduced for the successive coordination of the BuS-group (averaged reaction energy is -112.8 kJ/mol); 2) the adsorption energy is nearly independent on size of the cluster for the studied clusters, if the same coordination mode is considered; 3) energy of physical adsorption for BuSH (single molecular approximation) is remarkably lower than the corresponding dissociative adsorption;4) CO is an ambidentate ligand; 5) coordination through carbon atom onto Pt cluster surface is thermodynamically highly favorable with respect to coordination through oxygen atom; 6) two-and four-fold coordination modes were determined for CO adsorption through carbon atom onto Pt\{100\} model surface. In the later case, three bond lengths are about of 2.22 Å while the fourth one is about 2.41 Å; 7) the IR vibrational shifts for the stretch mode of CO (sharp mode in the simulated IR-spectra) due to adsorption are -200 cm^{-1} and -330 cm^{-1}, respectively to the adsorption mode; 8) CO can compete with BuSH for the adsorption site even in the single molecular approximation; however, in case of the dissociative adsorption it can compete with the second and successive coordination by the BuS-group; 9) bridge, planar, and vertical coordination modes of the aldehyde molecule adsorbed onto Pt(3x3) square (the upper layer of the Pt_{25}) either croton or acrolein were determined in the single molecule approximation (this translates to 1/9 ML coverage in the experiments with non-capped Pt NPs); 10) for bridge-like coordination of croton (anty-conformer) and acrolein, comparable adsorption energies were determined to be similar for the Pt\{100\} facet; 11) planar coordination either croton aldehyde or acrolein is thermodynamically more favorable in respect to bridge-like and vertical modes of coordination.

O.B. Gadzhiev is thankful for the partial support of this study provided by a grant under agreement of N.I. Lobachevsky State University of Nizhny Novgorod and the Ministry of Education and Science of the Russian Federation.

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Ethylation of toluene on La-modified HZSM-5 zeolyte catalysts

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Effect of lanthanum concentration on the adsorptive, acidic and catalytic properties of H-ZSM-5 in the toluene ethylation reaction was investigated. Influence of modifying on catalytic properties of HZSM-5 zeolite is studied in a 300-400^{0}C temperature interval. Under these conditions on H-ZSM-5 selectivity of p-ethyltoluene was made by 40,1-47,3%. It is established that increasing concentration of lanthanum on H-ZSM-5 makes reduction of porous volume, essential decrease in concentration of the strong acid centers that in turn leads to increase selectivity on p-ethyltoluene. By the increase in concentration of lanthanum in H-ZSM-5 to 10,0 wt. % selectivity on p-ethyltoluene increases from 42,3 up to 80,5%. The protonic parent HZSM-5 zeolite was obtained by ion-exchange of the commercially available ZSM-5 with NH_4Cl. The H-form of the zeolite was prepared by thermal decomposition of the NH_4 -form at 500°C for 4 h. The catalysts modified by introduction of 1.0–10.0 wt.% of lanthanum were prepared by impregnating the zeolite H-form with a solution of lanthanum nitrate at 80°C for 6h. The samples obtained were dried in air for 16h then for 4 h in a drier at 110°C, and then they were calcinated in a muffle furnace for 4h at 550°C. The La-loading of these catalysts was measured by atomic absorption spectrophotometer XRD. The specific surface was calculated according to BET method. The volume of pores was evaluated by t-plot analysis of the adsorption izoterm.

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Transmission electron microscopy investigation of Ziegler systems nature in arene hydrogenation catalysis: nickel systems

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The possibility of arene hydrogenation on Ziegler systems has been described in several articles [1, 2]. The other fundamental research about this topic are practically absent in the literature.

The report presents the results of studies of nickel Ziegler system based on $Ni(acac)_2$ – $4AlEt_3$ that are active in benzene and its methyl homologues hydrogenation by the high resolution transmission electron microscopy (HRTEM) in combination with electron diffraction. The size and nature of the nanoparticles forming in such system were determined. Its elemental composition was analyzed.

It has previously been shown [3, 4] that formation of the particles in benzene solution during interaction of $Ni(acac)_2$ with $AlEt_3$ at ambient temperature and pressure was not recorded by TEM.

During the hydrogenation of benzene in an autoclave at T = 120 °C and P = 15 bar of H_2 for 40 min there was particles formation the size of which varies from 0.6 to 2.5 nm. The average size of the particles was 1.38 ± 0.33 nm. The inter-lattice distance of 2.0511, 1.6671, 1.4437, 1.2913 Å, obtained by the electron diffraction, are similar to those of Ni (# 00-004-0850). Although it cannot be excluded that such inter-lattice distances can also correspond to various nickel aluminides, for example, NiAl (# 00-044-1188). The HRTEM image analysis shows the inter-lattice distances of 2.032 – 2.04 Å that correspond the planes both (111) of the Ni (2.034 Å # 00-004-0850) and/or (110) of the NiAl (2.0413 Å # 00-044-1188).

Sample from the reaction mixture at 80 minutes after the start of hydrogenation, is characterized by the presence of particles with the average size of 2.12 ± 0.10 nm. The particle size varied from 1.4 to 3.2 nm. Analysis of the data that obtained by both of electron diffraction and HRTEM shows that nanoparticles are correspond to the clusters of nickel or perhaps different types of NiAl. The increase of the particle size could be due to diffuse aggregation. The elemental microanalysis of the different fields of sample indicated the presence of Ni, Al, O, and C.

It was shown that the catalyst formed on the basis of the $Ni(acac)_2$ reduced only by hydrogen is 25 times less active in benzene hydrogenation catalysis than system based on $Ni(acac)_2$ – $4AlEt_3$ that consists mainly of nickel particles (inter-lattice distances of 2.0382, 1.744, 1.2812, 1.0789 Å are similar to those of Ni (# 00-004-0850)) and NiO (inter-lattice distances of 2.4186, 2.1126, 1.4793, 1.3884 Å are similar to those of NiO (# 00-044-1159)). The NiO is probably formed by atmospheric oxygen oxidation of the sample in the course of its installation in the microscope. The particle size commensurate with the size of particles formed in the $Ni(acac)_2$ – $4AlEt_3$ system according to the data of electron diffraction. By the HRTEM it was shown that in the absence of the stabilizer, the role of which performs the $AlEt_3$ and the products of its transformation [3], the particle agglomeration into clusters of size to 200-300 nm is take place. The elemental microanalysis of the different fields of sample indicated the presence of Ni, O, and C.

This work was supported by a base part of Government Assignment for Scientific Research from the Ministry of Education and Science, Russia (№2014/51, project code: 627). The TEM studies were carried out on the equipment of Baikal Nanotechnology Center (Irkutsk National Research Technical University, Irkutsk).

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Transmission electron microscopy investigation of Ziegler systems nature in arene hydrogenation catalysis: cobalt systems

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The mechanism of cobalt Ziegler catalyst systems formation at room temperature and atmospheric pressure were discussed in detail in our work [1]. So the report presents the results of research of cobalt Ziegler systems based on $Co(acac)_2$ – $3AlEt_3$ and $Co(acac)_2·2H_2O$ – $3AlEt_3$ that active in arene hydrogenation catalysis (T = 120 °C and P = 15 bar H_2) by the high resolution transmission electron microscopy (HRTEM) in combination with electron diffraction and X-ray microanalysis. The size and nature of the nanoparticles forming in the systems were determined, and was analyzed its elemental composition.

During the benzene hydrogenation in the autoclave at T = 120 °C and P = 15 bar of H_2 in the presence of the system $Co(acac)_2·2H_2O$ – $3AlEt_3$ for 60 min there was a particles formation. The size of the particles varied from 0.71 to 1.35 nm. The average size of the particles was 0.88 ± 0.16 nm. Analysis of the data that obtained by both of electron diffraction and HRTEM shows that nanoparticles are correspond to cobalt clusters. The elemental microanalysis of the different fields of sample indicated the presence of Co, Al, O, and C.

It has previously been shown [1] that formation of the particles in benzene solution during interaction of $Ni(acac)_2$ with $AlEt_3$ at ambient temperature and pressure was not recorded by TEM.

In the sample, taken after 60 min of benzene hydrogenation in an autoclave at T = 120 °C and P = 15 bar of H_2 amorphous matrix consisting of Al, C and O according to elemental analysis was identified by the TEM as well as impregnations in the matrix, having a certain degree of crystallinity. Accurate estimate of such areas is not yet possible, although the analysis of diffraction pattern shows that the size of generated particles in a given system is comparable to the size of the particles that formed in the system on the basis of $Co(acac)_2·2H_2O$ – $3AlEt_3$. Moreover, detailed treatment of the diffraction pattern of the consideration areas is indicates the presence of the following inter-lattice distances 2.4770, 2.1681, 1.5249, 1.3545 Å that are similar to those of inter-lattice distances Co [2.62348 Å (111), 2.272 Å (200), 1.60655 Å (220), 1.37007 Å (311), # 00-042-1300]. The elemental microanalysis of the sample indicated the presence of Co, Al, C and O. Also the individual nanometer size particles were registered. The diffraction pattern of the containing these particles area is described by the following inter-lattice distances 3.6498, 2.7911, 2.0916, 1.8289, 1.5686, 1.3684 Å that are similar to those of inter-lattice distances $AlCo_3C_{0.5}$ [3.7 Å (100), 2.616 Å (110), 2.136 Å (111), 1.85 Å (200), 1.6547 Å (210), 1.3081 Å (220), # 00-029-0023].

Analysis of HRTEM image indicates the presence of the inter-lattice distances 3.55 – 3.65 Å, that corresponded to the (100) plane of $AlCo_3C_{0.5}$ (3.7 Å # 00-029-0023), which confirms the data obtained by electron diffraction. Probably, formation of $AlCo_3C_{0.5}$ occurs under the action of the electron beam in the process of shooting of the sample in the electron microscope.

This work was supported by a base part of Government Assignment for Scientific Research from the Ministry of Education and Science, Russia (№2014/51, project code: 627). The TEM studies were carried out on the equipment of Baikal Nanotechnology Center (Irkutsk National Research Technical University, Irkutsk).

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Analysis of chemical composition and textural characteristics of platinum-rhenium catalysts samples

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Catalytic reforming is the major processin modern refining, which yields high-octane components of motor fuels. The quality of the product depends on the most important component of this process - the catalyst. The main criteria for the work of reforming catalysts areactivity, selectivity and stability of their work. The introduction of third-generation polymetallic catalysts helped to increase the production of high-octane fuel. Moreover, it allowed extending the cycle between regenerationsfor the catalyst volume more than twice.

For a comprehensive analysis of the catalyst, two different groups of methods are used. The first group are kinetic methods, that’s are usually used to explain the formal mechanism of the reaction, to show physico-chemical mechanism of specific processes and provide baseline data for the sound management of all production and process with its implementation, to determine the kinetic parameters of the reactions. Another group is called instrumental methods, that allow to determine the structure of the reaction surface of the catalyst and the composition of the active center of the direct reaction, a form of the reactants activation, and most importantly, to justify the mechanism of surface reaction on this platinum contact.

Based on the foregoing, one of the stages of the reforming catalyst research was to analysis of the chemical composition and structural characteristics of Pt-Re catalyst, which was used in the real fuel production. The analysis results were obtained using a scanning electron microscope JSM-7500FA. These results has given an opportunity to evaluate the uniformity of the various elements on the surface of the sampledistribution.

In the preparation of the catalyst during the dispersing step, the active components are distributed evenly across its surface. However, some elements can enter the porous structure of the catalyst from the outside and reduce its efficiency. It causes blocking of the pores or poisoning of the catalyst surface, i.e. the formation of local clusters that cover the active elements.

This effect can be observed when comparing the two catalyst samples taken before and after the working cycle. For example, aluminum is the most important component of the platinum-rhenium catalysts, the so-called support or matrix. Its concentration in the amount is up to 99% by weight. In the figure that shows the detailed structure of unused catalyst it can be seen that all the components are uniformly distributed. However, in the figure that shows the texture of the been-in-use catalyst we can see big surface portions that are covered by other elements. More detailed analysis showed that these portions are covered with iron.

However, the processing of the experimental data with the help of special software allowed to translate the visual characteristics of the experimental samples into numerical and directly evaluate the content of a particular component. The calculations showed that the content of iron on the surface of the catalyst reaches 0.37 wt.%, while it should not exceed 0.02 wt%. at average rates.

Thus, the detailed analysis of catalyst properties can help prevent the premature loss of the catalytic properties and increase the catalyst lifetime. This, in turn, will reduce the costs for regeneration of the catalyst components and to obtainbetter quality motor fuels with less investment.

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SECTION 4

INDUSTRIAL IMPLEMENTATION OF CATALYTIC PROCESSES

Partial oxidation of methane to synthesis gas over structured catalyst based on porous nickel: Effect of pressure and excess air ratio

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Addition of synthesis gas to the natural gas in an amount of 10-15% leads to greater uniformity of the combustion of fuel in the combustion chamber of gas turbines, a significant reduction in the emission of NO_x and CO. Stability of the process of partial oxidation of methane (POX CH_4) with air for catalytic reformer of gas turbine power plant is a crucial issue. Overheating of the front point of the catalyst bed (hot spot) leads to instability of the process because of possible catalyst sintering and destruction [1]. For the industrial realization of this technology it is necessary to study the catalytic process POX CH_4 at elevated pressures.

In this work, we investigate the effects of pressure (P = 2, 4, 6 atm.), excess air ratio ($\alpha=O_2/2\cdot CH_4$ = 0.32; 0.37; 0.42), gas hourly space velocity (GHSV = 19900 - 49500 h^{-1}) on the temperature in the front point of the structured catalyst. Also comparison of the composition of reaction products with thermodynamically equilibrium was done. We used an in-house made catalyst based on porous nickel stripes (trade mark eK0.021.742TU Type 2).Using MgO support for nickel catalysts leads to the formation of a solid solution NiO-MgO, which potentially may increase the catalytic activity by highly dispersed nickel particles which are generated after Ni reduction from solid solution. It was reported that small Ni clusters (<6 nm) prevent catalyst coking [2], but unfortunately the degree of Ni reduction from its solid solution with MgO may be very low. So, the preparation of such a catalyst is a challenging task. Our catalyst 14,4%NiO-7,7%MgO/porous Ni demonstrated the lowest hot spot temperature in POX CH_4, among such catalysts with different loadings of NiO and MgO. The sample was in the form of structured cylindrical monolith formed from alternating flat and corrugated porous Ni tapes.

According to our experimental results: (1) increasing the pressure leads to a reduction in the temperature of the frontal point of the catalyst, (2) increasing the air excess ratio α leads to an increase in methane conversion (which is consistent with [4]), and increases the inlet hot spot temperature; the effect of α on the temperature of the frontal point decreases with increasing pressure, (3) increasing GHSV leads to an increase in the temperature of the frontal point of the catalyst (this effect was also observed by the authors of [3]). According to reports [3-5] the process POX CH_4 can be divided into three parallel reaction pathways: combustion (exothermic), steam reforming (endothermic) and reverse-shift reaction (slightly endothermic). Our experimental results can be describe by model, in which CH_4 combustion takes place in the external diffusion control by O_2 and is independent from pressure [3-5] from 1 to 8 atm. CH_4 steam reforming, according to our model, occurs in a mixed chemical-diffusive control by CH_4 (which is similar with report [5]), but is closer to external diffusion than kinetic regime. The experimental compositions of reaction products are close to the thermodynamic equilibrium (calculated according to this model), so it can be argued that the process of POX CH_4 at the monolith outlet occurs near the thermodynamic equilibrium. This is a good prerequisite for future testing of this catalyst in a full-scale industrial catalytic reformer.

This work was carried out on state assignment V.44 for Boreskov Institute of Catalysis.

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The Prospects of Industrial Catalytic Oxidation of Cyclohexane

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The selective oxidation of cyclohexane (CH) to cyclohexanone (ANON), cyclohexanol (ANOL), cyclohexyl hydroperoxide (HPCH) is a key stage for the industrial production of caprolactam, adipic acid (ADA) and some other valuable products of large-tonnage organic synthesis. More than 95% of ANON is used in the production of ε-caprolactam, which in its turn is used to manufacture polyamide and wide range of chemical products, including synthetic fibers, engineering plastics, and films. Global production of polyamides reaches more than 3 million tons per year. In industry the liquid phase oxidation of the CH is carried out 150-160 ºC and 5-10 atm. in the presence of a catalyst or in an autothermic mode. The CH conversion does not exceed 4-6 %, while the selectivity towards ANOL and ANON together reaches 75-80 %.

Patent searches as well as other open information sources show that the interest in CH oxidation has not been falling for the last 20 years. A large number of studies is directed towards the increase of the reaction rate of CH oxidation and rise in selectivity towards the main products. The most active applicants from the observed documents are JCS "Kujbyshev Azot" (Russian Federation) and Vista Technologies (the Netherlands), while the most numbers of utility patent applications worldwide belong to China, USA, Japan, Russia, and international applications.

Modern trends in CH oxidation technology development are as follows:

1. search for an effective homogenic/heterogenic catalytic composition allowing users to increase the CH conversion without substantial loss of the selectivity towards the main products, i.e. ANON and ANOL;
2. reveal a highly efficient combination of transition metal cations contained in a catalytic composition providing the preferential formation of the ANON in the products of CH oxidation;
3. elaboration of the catalysts for selective decomposition of HPCH up to ANON;
4. creation of a new technologic methods directed on the rise of contact between the oxygen-containing gas and CH with application of several zones for introduce of gas mixture;
5. elaboration of combining contact apparatus with rectification of valuable products;
6. improvement of the technology of product mixture treatment, etc.

According to our experimental results for microscale laboratory device the usage of the bicomponent catalytic systems on the basis of N-hydroxyphthalimide derivatives and transition metal salts allows increasing the growth of the CH conversion more than 2 times per single cycle, while the selectivity towards ANOL and ANON remains unchanged. It is important that the formation of the resins and other oligomer compounds is not observed. The results of computer modelling and preliminary calculations show that the application of the proposed catalytic system allows decreasing the specific heat load in rectification columns of the recycled CH to up to 60 %. Moreover, we expect a decrease of the waste up to 30 %.

In the present work the results of computer modelling will be presented for comparison with the real technological process. The prospects for the development of the imide catalysts for oxidative processes in industry will be discussed.

Catalyst for air regenerative products

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Air regeneration in a self-contained breathing apparatus is based upon the use of chemical product which generates oxygen in the reaction of potassium superoxide with water vapors and carbon dioxide contained in exhaled air.

Different structure-forming additives and catalysts are often included in the composition of an air regenerative product to enhance the diffusion of water vapors and carbon dioxide inside the granules of the shape product. As such additive it is suggested the use of alkali metal ferrates (VI) which can be obtained by self-propagating high temperature synthesis [1, 2].

It is found that during the process of air regeneration in the presence of alkali metal ferrate (VI) the autocatalytic type reaction takes place. Ferrate (VI) reacts with moisture resulting in formation of iron (III) hydroxide, $Fe(OH)_3$, which catalyzes the decomposition of potassium superoxide [3].

The tests of the regenerative product composition comprising ferrate (VI) catalyst in the rebreather system showed higher conversion of the regenerative product, reducing the concentration of carbon dioxide in inhaled air and elongation of operation time of the apparatus.

The regenerative products comprising ferrate (VI) catalyst are promising for commercial production.

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Realization of highly exothermal processes in micro-channel reactors: experimental studies and mathematical modeling

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The studies of catalytic processes in the micro-channel reactors have received great attention in the last years. Due to the small sizes of reaction zone, such types of reactor have some advantages, in particular, high efficiency of heat and mass transfer. This benefit plays important role if the process is accompanied by substantial heat release, or heat consumption.

The paper is devoted to experimental and theoretical studies of highly exothermal process of methanol to formaldehyde oxidation in micro-channel reactor. The reactor consists of 5 plates with Fe-Mo catalyst. The plate length is 40 mm. Each plate contains 4 channels, 0.4 mm height and 5 mm width. The distance between channels is equal 2 mm. The reactor is heated up to the temperature of reaction in the flow of inert gas. The temperature in the outlet of the reactor is kept at a constant value by regulating the power of the furnace. The oxygen to methanol ratio is 1.5. We studied the influence on methanol conversion and formaldehyde selectivity of the parameters as follows:

- The temperature variation at the reactor outlet from 240 to 340°C. Inlet methanol concentrations are 6.5 and 12 vol.% at two different mixture flow rates 26250 and 52500 h^{-1};
- The mixture flow rate variation in the inlet of reactor from 10000 to 65625 h^{-1}. Inlet methanol concentrations are 6.5 and 12 vol.% at constant temperature value at the reactor outlet 300°C.

Mathematical simulation is done on the base of two-phase model. The model takes into account the convective heat and mass transfer in the gas phase of the reactor channels, change of both concentrations and temperature due to reactions in the solid phase of the plates, the heat exchange with oven and axial thermal conductivity of the solid phase of the plates, heat and mass exchange between gas and solid phases. The inlet concentrations are given. The inlet temperature was set so that the outlet temperature would coincide with experimental one.

We obtain a good agreement between calculated and experimental data. We reveal that under fixed values of the gas flow rates 26250 and 52500 h^{-1}, temperature increase in the reactor outlet from 240 to 340 °C results in the rise of methanol conversion for both values of inlet methanol concentrations 6.5 and 12 vol.%. The mixture flow variation at 300°C in the reactor outlet shows that under low value 10000 h^{-1} the methanol conversion comes to 97-98% for both inlet methanol concentrations. The increase of the value up to 65625 h^{-1} at the same temperature in the reactor outlet leads to fall of conversion up to 44 and 39% under 6.5 and 12 vol.% of the inlet methanol concentrations, respectively. This is connected with insufficient residence time in the reactor for complete conversion, especially in the case of larger value of inlet methanol concentration.

This work was supported by RFBR Grant 15-08-02963.

A Catalytic heater for external combustion engine

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In many types of heat engine devices a combustible fuel is employed and its heat of combustion is transferred to a working fluid for conversion. A common type in widespread current use employs an open plasma flame as the transfer medium. Another type employs a flameless combustion process that utilizes a catalytic coating at the surface area where heat is to be applied. In practice, an increase in the flow of thermal energy being transferred to the external heat engine is the primary mechanism for improvement of its performance. At the same time, it is known that syngas (mixture of H_2 and CO), which can be prepared by the conversion of natural gas, is catalytically oxidized very easily. We hereby propose a dedicated catalytic heating element (CHE) that promotes the catalytic combustion of syngas, thus generating the primary source of thermal energy input for an external heat engine device.

A detailed presentation of the CHE device can be found in Ref. [1] nevertheless, a brief overview of the proposed design is provided here for completion. In order to promote the CHE is a cylindrical structure consisting of an annular tubular heat exchanger, which is located inside a gas distribution perforated tube where the premixed air-fuel mixture is supplied to the element. Uniform distribution of the fuel mixture and the extension of the mixture jets issuing from the holes around the gas distribution pipe, a perforated splitter is introduced around the fuel mixture supply tube. The catalytically active layer has a regular structure, and is composed of five flat and corrugated strips, wound on the tube heat exchanger and sintered together. The thickness of the strips is about 1 mm with the winding pitch on the tube heat exchanger amounts to 27.5 mm. Tapes permeable to the gas form catalytically active channels with a diameter of 2.5 mm. The width of the tapes is 25 mm, and the spacing between adjacent rows of winding is 2.5 mm. The first and last rows are formed by flat ribbons, while the intermediate layers consist of alternating flat and corrugated strips. To reduce the heat losses, the catalyst layer exceeds beyond the length of the heat exchanger. Furthermore, in order to reduce the start-up time of the heating element, the outer layer of the catalyst has a size larger than the critical size of ribbed channels for the penetration of flame into the porous structure. The concentrations of the components in the fuel mixture were measured by a GC (Crystal-2000M), and the concentrations of CO and NO_x in the exhaust gases were measured by a gas analyser (KM-900).

This process is carried out on reinforced metal porous catalysts produced by self-propagating high-temperature synthesis. According to X-ray analysis, composite catalyst comprises the following phases: Ni, α-Cr_2O_3 and α- Al_2O_3. The specific surface area of 3.4 m^2/g; catalyst characterized by macroporous structure: a main pore volume in pores with a radius from 15 to 100 microns.

The use of the aforementioned CHE device for the catalytic combustion of natural gas (here mainly methane, 86 – 98% by volume) allows the heating power and temperature to be regulated over broad ranges by suitable adjustment of the air-fuel ratio in the mixture. The use of such a CHE allows the generation of a high-intensity, uniform heat flux, and therefore, its employment acts to promote the intensification of the heat transfer process to the external combustion engine. In fact, it has been shown that the overall engine system efficiency can be increased to 30-35%, and by using thermochemical recuperation up to 41% [3]. Furthermore, it is evident from our current results that the syngas is generated at the desired ratio of 1:2 and that the concentration of CO and NO_x within GOST levels.

This research was performed under the UNIHEAT project. The authors wish to acknowledge the Skolkovo foundation and BP for the financial support.

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Development of technology of hydrocracking vacuum distillate on the basis of domestic catalysts

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Hydrocracking is one of the most quickly developing processes of the oil refining. Several units of hydrocracking of vacuum distillate on the basis of foreign catalysts and technologies are operated in Russia today.

Research of production of petrol and diesel fractions using the industrial aluminium-nickel-molybdenum catalyst in process of hydrocracking of vacuum distillate is performed on JSC “AC&OSP ” within import substitution program.

Tests was carried out at a temperature of 380-420 °C, pressure of 15 MPa, feed space velocity 0.3-8 h-1 in a pilot flow reactor with volume 100 cm3. As raw materials used viscous vacuum distillate (FBT of 530 °C).

As a result of this work the optimal technological parameters of the process of hydrocracking are determined.

It is shown that catalyst allows to produce light oil products with total yield about 57 % wt. (terms of feed) at a temperature of 400 °C, feed space velocity 0.5 h-1 and at a temperature of 420 °C, feed space velocity 0.8 h-1, losses of raw materials as hydrocarbon gases – 20 % wt. The yield of petrol fractions are equaled 29-33 % wt. and diesel fractions are equaled 39-44 % wt.

The density and content of sulfur of the petrol fractions correspond to quality of GOST R 51886-2002 “Unleaded petrol”, octane number is equaled 70-72.

The characteristics of the diesel fractions correspond to quality of GOST R 52368-2013 “Diesel fuel EURO”:

- type II according to sulfur content;
- class 0 according to low temperature propeties.

The breakdown product represents deep treated low viscous fraction with viscosity 3.7 mm2/sec at 100 °C, flash point – 177 and 209 °C, pour point temperature 6 and 9 °C, content of sulfur 0.0012 and 0.0027 % wt.

Tests are carried out within 1224 hours, that characterizes stability of catalytic properties in this process.

Process of propylene production by propane dehydrogenation on catalysts of JSC RI “Yarsintez”

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For many years JSC RI “Yarsintez” has studied and developed the process of propylene production by propane dehydrogenation in fluidized catalyst bed. It has been found that using for this process the modifications of industrial catalysts for the dehydrogenation of paraffins provides high catalytic performance at pilot plant of JSC RI "Yarsintez" [1] for a long time (more than one year), nevertheless insufficient to compete with other industrial processes.

Eventually JSC RI "Yarsintez" has developed the novel original catalyst IM-2212 for propane dehydrogenation process. It has higher catalytic characteristics. The effect of temperature and volumetric feed rate on the performance of dehydrogenation process was studied in the wide range. The effect of temperature and volumetric feed rate on coke formation on catalyst IM-2212 in propane dehydrogenation process was studied.

Process of ИМ-2212 catalyst production has been developed. Optimal process-dependent parameters of propane into propylene dehydrogenation process on the new catalyst have been determined. Mathematical model of reactor and regenerator has been specified, besides, the new reactor design providing stable operation at high feed rates has been proposed.

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Elaboration of the protective covering of walls of reactor for ethylene glycol oxidation process

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In industry glyoxal is produced by vapor-phase oxidation of ethylene glycol on silver catalysts. Novel catalysts with low silver loading (up to 4%wt), which were created in Laboratory of Catalytic Research of Tomsk State University, allow producing the 30-34 %wt glyoxal solution for one cycle with selectivity towards glyoxal of 75 % at 99 % ethylene glycol conversion [1]. It is necessary to note that these results were observed in quartz reactor. Preservation of similar parameters in industrial scale would significantly increase the production effectiveness. It is obligatory to use a protective covering on the walls of reactor, evaporator etc to provide the required conditions.

It is known that metal surfaces of evaporator and other walls of apparatus influence negatively on the process, and usually the glyoxal yield is decreased. Creation of “inert” covering would allow both decreasing of reactor cost and increasing of glyoxal yield.

To perform laboratory investigations small reactors are commonly used. The ratio between the volume and the wall surface in such reactor is significantly higher in comparison with industrial apparatus. Hence, influence of hot metal surfaces must be considered for laboratory or pilot reactor scale. Another important factor is the increase of reliability for the research results, which requires to make sure that the covering of reactor walls are inert. In this study the research results of ethylene glycol transformation with the use of titanium foil with a protective covering prepared via microplasma oxidation [2] are presented.

To establish the role of the covering in ethylene glycol transformation the results were compared to the data obtained in a flow quartz reactor. It was shown that the composition of the used complex oxide coating on titanium foil significantly influences on the reagent conversion, with the one for the alcohol reaching 70% under 650 ^{o}C. The titania-based coating showed results comparable with the quartz reactor data without a catalyst, which indicates its inertness towards the featured reagents (oxygen, ethylene glycol) as well as prospect of using such coating in producing construction materials used for high temperature oxidation including the studied process.

This work was supported by The Tomsk State University Academic D.I. Mendeleev Fund Program in 2016.

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Testing results of catalysts using mathematical model of catalytic cracking

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At present, the overwhelming majority of catalytic cracking units operate using synthetic microspheric zeolite catalyst [1-2]. The testing results of the cracking zeolite catalysts using the mathematical model of catalytic cracking developed at the Department of Fuel Engineering and Chemical Cybernetics of Tomsk Polytechnic University are given in this research

The aim of this research is to evaluate the effect of the catalyst type on the yield and distribution of the main products of catalytic cracking during vacuum distillate conversion with a high content of saturated hydrocarbons.

The object of research are industrial catalysts (CAT-1 and CAT-2) used in the catalytic cracking units. CAT-1 catalyst is characterized by a high content of zeolite components (Y and ZSM-5) – 31.5 and 12.0 % wt. relative to the catalyst CAT-2 (20 and 2 % wt.). The zeolite ratio ZSM-5 to Y is 0.381 for the CAT-1 catalyst and 0.11 for the CAT-2 catalyst.

The mathematical model is based on the formalized scheme of hydrocarbon conversion in accordance with the results of the laboratory research by determining composition of feedstock and products and thermodynamic analysis of the catalytic cracking reactions using the methods of quantum chemistry [3].

The calculations were performed at the constant parameters of the technological mode (temperature at the exit of the regenerator zone is 690.0°C, feedstock flow rate is 378.0 m^3/h, feed temperature is 304.0°C, slops flow rate to the reactor is 9.2 m^3/h, steam flow rate in the grip of the riser reactor is 5500.0 kg/h, the catalyst circulation rate is 5.56 ton_{cat}/ton_{feed}). The ratio of saturated hydrocarbons to aromatic hydrocarbons in the vacuum distillate is 2.1, the content of alcohol-benzene resins is 3.5 % wt., and feedstock density is 0.904 kg/m^3.

The calculation results are showed that the yield of wet gas is significantly higher in case of the operating CAT-1 catalyst (38.53 % wt.), than in case of the CAT-2 catalyst (16.8 % wt.), due to a high content of the ZSM-5 zeolite at CAT- 1 catalyst composition, which provides high selectivity of the secondary cracking reactions of gasoline hydrocarbon with wet gas formation. At the same time the coke content on the CAT-1 catalyst is above (0.94 % wt.) relative to the CAT-2 catalyst (0.78 % wt.), which is associated with a high rate of condensation reactions in the wide pores of the Y zeolite. Wet gas of the CAT-1 cracking catalyst is characterized by a high content of propane-propylene fraction (37.07 % wt.) relative to the wet gas produced during operation of the CAT-2 catalyst (31.50 % wt. with a low content of the ZSM-5 zeolite).

Gasoline fraction is characterized by a high content of olefinic hydrocarbons (19.53 % wt.) during CAT-1 operation because the catalyst has a lower content of ZSM-5 zeolite, and for this reason the cracking reactions of olefins from gasoline with gas formation occur less. The content of aromatic hydrocarbons in the gasoline is significantly higher during CAT-1 operation (42.36% wt. – CAT-1 and 34.29% wt. – CAT-2), which is associated with a high rate of aromatic hydrocarbons dealkylation and olefins aromatization, that is characteristic in case of a high content of the high-porosity Y-zeolite.

The content of isoparaffin hydrocarbons in gasoline is above in case of CAT-2 operation that is characteristic for the low ratio of the ZSM-5/Y zeolite (0.11). Therefore, the reaction rate of hydrogen redistribution is high. The high content of aromatic hydrocarbons in gasoline in case of CAT-1 provides a high octane number (93.8 RON). The gasoline fraction during CAT-2 operation is characterized by a high content of isoparaffinic hydrocarbons (91.35 RON).

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Chlorinated alumina: Effect of alumina interaction with CCl_4 on their morphology and surface acidity

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Chlorinated alumina catalysts containing 2-10 wt.% Cl and 0.2-0.5 wt.% Pt are widely discussed as catalyst for low-temperature hydroisomerization and alkylation of C_4-C_6 alkanes [1-3]. The activity and stability of the chlorinated alumina in these reactions is known to depend on the surface acidity [3,4], which is controlled by chlorine content [4]. Chlorinated alumina are early prepared by alumina interaction with CCl_4 at 300 °C [5], $AlCl_3$ at 500 °C [6] or HCl at 650-700 °C [7]. Here, we are reporting our systematic study of the effect of chlorination procedures into the textural characteristics, particles size, particles morphology and acidic properties of chlorinated χ-Al_2O_3 catalysts.

We are discussing regularities of chlorine anions sorption by alumina from CCl_4 as function of CCl_4 concentration, temperature and time. At the same temperature (300 °C), the sorption of chlorine anions by χ-Al_2O_3 was shown to be well described within the Langmuir monomolecular adsorption. Sorption capacity of χ-Al_2O_3 was equal 560±15 mkmol Cl/g, it reached at passing of CCl_4 (1.5 vol.%) through catalyst bed. This value by 4 times exceeds concentration of the basic Al-OH groups which are characterized by bands located at 3795 and 3775 cm^{-1} of FTIR spectra. The basic Al-OH groups are believed [4,8] to be primarily exchanged with the chloride ions.

When step-by-step modification of alumina by NH_4Cl and CCl_4 was used, the Cl-content was shown to be additively increased. It is because HCl formed at NH_4Cl thermal decomposition reacts with the surface Al–O–Al groups, increasing total amount of Al-Cl groups.

Chlorination temperature that was changed from 200 to 500 °C had a nonlinear effect on the chlorine content in the alumina and their morphology. It is due to different route of CCl_4 decomposion over Al_2O_3. At 300 °C and below, there is reaction between CCl_4 and surface Al-OH, resulting in alumina modification by Cl-anions and carbon deposit. The textural properties and particles size/morphology of alumina chlorinated at 300 °C were similar to those of the pure alumina. At 400 °C and above, CCl_4 transforms to $COCl_2$ and latter reacts with alumina, giving surface Al-Cl groups as well as $AlCl_3$ nanoparticles. So, here the smaller alumina particles compared with pure alumina were formed due to destruction of alumina lattice.

The surface acidity detected in the chlorinated alumina by FTIR-CO and TPR-NH_3 will be discussed. It was shown that chlorination of χ-Al_2O_3 by CCl_4 is a key factor in the improvement of its surface acidity associated exclusively with medium and strong Lewis acid site.

This work was supported by Russian Academy of Sciences and Federal Agency of Scientific Organizations, project # II.2П/V.45-12 (0303-2015-0006)

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An Influence of Wood Flour Additive on Porous Structure and Strength Properties of Moulded Alumina

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At present, there are strict requirements for industrial catalysts. The catalysts must possess both high activity and selectivity, be resistant to catalyst poisons, withstand to short-time overheating, and have high stability, including retaining of high catalytic activity and a longtime granule strength [1, 2]. Special attention is given to the porous structure of the catalysts because it determines the catalyst activity, stability, granule strength and other features. The properties of the supported catalysts are known to significantly depend on the support properties [3]. The preparation of supports and catalysts with desired porous structure is an important problem for both fundamental and applied catalysis. Thus, new methods to design the materials with controllable hierarchal nano- and macroporous structure must be elaborated [4, 5].

In the present work the methods to controlthe porous structure and strength properties of the alumina during its moulding by addition of the wood flour were proposed. Special attention was given to porosity due to nanopores providing high specific surface area and the stabilization of supported active component in a dispersed state. Wide macropores were shown to effectively transfer the reagents to the active sites of the catalysts and withdraw the products. The thermochemically activated $Al(OH)_3$ was used as an alumina precursor because of its high specific surface area and appropriate properties for moulding (e.g., high workability).

The alumina supports were prepared by mixing the thermochemically activated aluminum trihydroxide (TCA ATH) with an aqueous solution of HNO_3 and a wood flour. The wood flour was used as a pore agent with a loading from 0 to 5 %wt. Then the wetting viscous mass was formed by the extrusion. The resulting cylindrical granules with diameter of ~3 mm were dried at 100 °C for 12 hours and calcined in air at 750 °C for 4 hours. A series of Al_2O_3 supports with different wood flour loading (0, 2 and 5 %wt.) were studied by the SEM, low-temperature N_2 sorption, XRD, granule strength and water-absorbing capacity methods.

It was shown that the alumina supports, prepared from thermochemically activated aluminum trihydroxide precursor, had both high stability and developed porous structure. All supports represented γ-Al_2O_3 phase, making them promising materials for various applications. It was shown that addition of the wood flour led to increasing the porosity of the support including broadening of the nanopores and significant reorganization of structure of the pores with sizes of several micrometers. It was found that the increasing of the wood flour addition led to formation of a well-developed structure required for the catalyst. There was an insignificant increase of the total pore volume and a reduction of the specific surface area for supports with a wood flour in comparison with the alumina support without wood flour additive. The addition of a big amount of wood flour (5 %wt.) led to significant reduction of the strength of the support granules.

This work was supported by the federal target program "Research and Development in the Priority Areas of the Science and Technology Complex of Russia for 2014–2020" (contract no. 14.578.21.0028, RFMEFI57814X0028).

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Scientific edition

CATALYSIS: FROM SCIENCE TO INDUSTRY

Proceedings of
IV International scientific school-conference for young scientists
in memory of Professor L.N. Kurina

2016, October 23 – 27

All proceedings are published as is; maintenance responsibility remains to authors

Original layout by *V.S. Malkov*
Cover designed by *O.V. Kireeva*

It's published at "Ivan Fedorov" publishing as provided by original layout

Signed to print 20.10.2016. Format $60\times84_{1/8}$. Offset paper №1.
Offset print. Sheets 17,75. Relative sheets 16,51. Publisher's signature. 15,98.
Order №16581. Number of copies 20 issues.