CATALYSIS:
from science to industry

PROCEEDINGS OF
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Оборудование для определения площади поверхности, пористости, поверхностной энергии и других характеристик поверхности катализаторов методами динамической сорбции паров и обратной газовой хроматографии компании **SurfaceMeasurementsSystems, Великобритания** позволяет всесторонне использовать адсорбционные исследования для получения характеристик для оптимизации катализаторов. Для непористых поверхностей различные составляющие поверхностной энергии можно определить с помощью тензиометров и оптических измерителей краевого угла компании **Dataphysics, Германия**.

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PLENARY LECTURES

Adsorption and catalysis for renewable and sustainable energy applications

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Nowadays, the main primary sources of energy are fossil fuels. The persistent trend towards the sustainable power production requires the replacement of fossil fuels with renewable energy sources and rational use of heat in industry, transport and dwellings (re-using exhaust heat, energy storage, etc). These new heat sources have a lower temperature potential that opens a niche for applying adsorption and catalytic technologies for energy transformation and storage. Indeed, both processes allow efficient conversion of chemical energy to heat and back (the so-called thermochemical energy conversion, TEC) [1-3].

The TEC thermodynamics is determined by an evolution of the Gibbs free energy ΔG in the course of energy converting process (catalytic reaction or adsorption). The Carnot efficiency η_{Carnot} can be reached in the case of a mono-variant reaction system, whereas for a bi-variant adsorption process the efficiency is lower than η_{Carnot} due to the entropy production caused by the thermal coupling between a reactor and an external heat source [4, 5]. Main factors affecting the efficiency have been analyzed [2, 5, 6].

The catalytic version of TEC (CTEC) is found to be more applicable for transformation of heat with the temperature potential higher than 200-300°C. The adsorption version (ATEC) is suitable for heat of low temperature potential (100-150°C), first of all, for renewable and waste heat sources. At present, huge amounts of this heat are unproductively dissipated to the environment [7]. Because of this strong motivation, so far ATEC has been more advanced than CTEC: many adsorption chillers/heat pumps were developed in the 21st century, and some of them have passed over from prototype stage to serial production [8].

These emerging technologies give the exiting ability to 1) use fossil fuel 30% more efficiently than current best practice (for heating), 2) utilize waste heat that is otherwise lost (100% saving of fossil fuel), 3) cool using low temperature renewables, 4) store waste heat for reuse, and 5) upgrade low temperature waste heat for industrial processes. This could reduce the consumption of fossil fuels by at least 25% [3].

Despite the recent progress, there is still a room for significant ATEC improvement by means of thermodynamic harmonization of the adsorbent and ATEC cycle to enhance the efficiency [9]; dynamic optimization of the ATEC unit to increase the conversion/storage power [10]; better cycle organization and the ATEC hardwire towards more simple and robust designs [11].

Innovative materials are a prerequisite for major breakthrough applications influencing our daily life, and therefore new efficient adsorbents and catalysts are pivotal for efficient TEC. Several relevant materials (zeolites, silica gels, metal-aluminophosphates, metal-organic frameworks (MOFs), ordered mesoporous silicas (SBA, MCM), activated carbons, and composites) are considered and compared.

Our analysis of the current state-of-the art and modern trends in TEC has demonstrated that new ideas, methods and materials emerging from basic research in catalysis and adsorption science will lead to pronounced breakthroughs and changes in the sustainable energy industry of the near future.

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Structural and chemical dynamic evolution of catalysts under gaseous environments in real-time at high spatial resolution

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Catalysts being generally very divided materials composed of active phase nanoparticles supported on powder supports, their catalytic performance (activity, selectivity, stability) is intimately related to their active phase surface properties (atomic and electronic structure, atom coordination and valence, chemical composition, segregation effects…) and in the way they dynamically evolve during the catalytic reaction. Surface science methods such as scanning tunneling microscopy (STM), polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS), X-ray photoemission spectroscopy (XPS), working under gaseous reactive environments [1-4], are thus well appropriated to obtain quantitative structural, electronic and chemical data on extended catalytic surfaces (single crystal, polycrystal, thin films, …). These are used as catalyst models from which it is possible to finely derive information on the influence of a given parameter on the catalytic behavior of such surfaces.

In order to progress in the understanding the mechanisms that control the behavior of the catalysts in a reaction, we must verify that the results obtained on extended surfaces can be extrapolated to finite catalysts and use this information to design better and more effective catalysts with specific controlled properties. The study, at a local scale, of supported or powder catalysts requires high-spatial resolution methods due to the nanometer scale of the materials. In this sense transmission electron microscopy (TEM) provides a platform within which it is possible to perform both imaging and spectroscopy at subnanometer and/or atomic level. Environmental TEMs have been developed for many years [5,6]; however, only recently the evolution of TEM platforms, namely aberration-corrected TEMs, opened the possibility of performing *in situ* real-time experiments in environmental conditions (P_{gas} up to 20 mbar and T up to 1000°C) while maintaining high spatial resolution capabilities [7].

Here we will show examples of studies performed in an environmental aberration-corrected TEM (the Ly-EtTEM of the CLYM, Lyon) under reaction conditions on dynamic real-time morphologic/structural and chemical evolution of supported catalysts with high-spatial resolution: (i) the evolution of the surface structure/chemical composition of ceria nanoparticles in presence of CO_2 or O_2; (ii) the dynamic real-time structural/morphologic/chemical modifications of silver nanoparticles supported on amorphous-carbon in presence of O_2 at high temperature. We also report on the tomographic capabilities of our microscope and especially on the fast (minute-level) 3D approach on catalysts under gaseous environments at variable pressure and temperature. Finally, issues dealing with the electronic beam interaction with the catalysts under environmental conditions will be addressed.

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Preparation of SiO_2/TiO_2 sol and its photocatalytic properties

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Titania has been extensively used as a photocatalyst. However, when TiO_2 is coated on glass, the light transmission is not high enough. This study aimed to investigate the synthesis of SiO_2/TiO_2 hydrosols with the different compositions of SiO_2, which possess high light transmittance and high photocatalytic activity simultaneously. The presence of SiO_2 in the films could inhibit the diffusion of sodium cations from the glass substrate to TiO_2 during heat treatment process. It also has antireflection and antiglare properties.

TiO_2 and SiO_2/TiO_2 hydrosols were prepared by peroxo sol-gel method by using $TiCl_4$ as precursor. It was found that the as-prepared TiO_2 sol was stable light-yellow transparent sol which contained the rhombus shape of TiO_2 nanoparticles dispersed in the sol. The high aspect ratio of TiO_2 particles and high surface area yielded high activity. The sol was neutral solution, instead of acidic solution. It had high dispersibility without adding any surfactant. In addition, the as-prepared SiO_2/TiO_2 sols showed that the TiO_2 nanoparticles were embedded in the spherical SiO_2 particles. This type of combination possesses some better advantages than the others due to the efficient reversible absorption of target organic substances and short traveling distance from the adsorbed site to the active one. For antireflection study, the films were prepared by dip-coating on glass in order to obtain the thickness of about 1 μm. It was found that the transmittance increased along with the presence of SiO_2 and could enhance the light transmittance up to 4% compared to the bare glass substrate. The presence of SiO_2 also could suppression the migration of sodium from glass to TiO_2. For the photocatalytic degradation of methylene blue aqueous solution, the bare TiO2 film had the highest activity among all the samples. Instead, based on the same amount of TiO2 species in the films, the presence of SiO_2 in the film could enhance the photocatalytic activity of TiO_2. SiO_2-TiO_2 film also has anti-finger print property.

Bi-functional TiO_2-SiO_2 sols with antireflection and degradation of organic dyes were prepared by using peroxo sol-gel method. This can be the alternative way to produce the film coating on substrate which possesses high light transmittance, prevents the sodium diffusion from substrate to film and preserves high photocatalytic activity simultaneously. By adding other metals, such as Ag and Au, it has antibacterial properties.

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The activity of TS-1: some considerations on its origin

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Following first applications of ammoximation in 2003 and HPPO in 2008, current world production of bulk chemicals, based on TS-1, can be estimated at ca. 300 kt/a of caprolactam (ammoximation) and of 1.2 Mt/a of propylene oxide, with other projects seemingly under way. Such a rapid growth is certainly due to a greater environmental awareness and the consequent stricter rules issued for waste production and disposal. The basic pillar, however, of the success of TS-1 is its catalytic effectiveness, on which three decades of studies coming from different groups allow reasonable considerations to be made and some conclusions to be drawn.

Different factors appear to contribute to the activity of TS-1. The nature of the surface (hydrophobic), the structure of Ti site (tetrahedral) and the nature of active species (Ti-OOH) are three obvious ones. Hydrophobicity alone, however, does not fully explain certain catalytic performances and trends in the oxidation of a range of substrates, without envisaging a positive role for porosity. Actually, the molecular dimensions of pores (ca. 0.55 nm), normally perceived as just a drawback for the range of potential substrates, can also play a positive role in TS-1 catalysis. The purpose of the presentation is to illustrate and discuss such issues, with supporting evidences mostly taken from the oxidation of olefins and alkanes.

Coherent synchronized oxidation reactions by hydrogen peroxide in aspect of the biomimetical catalysis

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Various types of possible interactions between reactions are discussed. Some of them are united by the general idea of coherent synchronized chemical reactions. The ideas on conjugated reactions are broadened and the determinant formula is deduced; the coherence condition for chemical interference is formulated and associated phase shifts are determined. It is shown how interaction between reactions may be qualitatively and quantitatively assessed and kinetic analysis of complex reactions with underresearched mechanisms may be performed with simultaneous consideration of the stationary concentration method. Using particular examples, interference of hydrogen peroxide dissociation and oxidation of substrates is considered.

The area between enzymatic and chemical catalyses, associated with simulation of biochemical processes by their basic parameters, is accepted as mimetic catalysis. The key aspect of the mimetic catalyst is diversity of enzyme and biomimetic function processes, which principally distinguishes the mimetic model from traditional full simulation. Based on the analysis of conformities and diversities of enzymatic and chemical catalysis, the general aspects of mimetic catalysis are discussed. The most important achievements in the branch of catalysis are shown, in particular, new approaches to synthesis and study of biomimetic catalase, peroxidase and monooxidases reactions.

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Isotopic-kinetic study of reactivity of surface oxygen species on oxide catalysts in partial and deep hydrocarbon oxidation

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Metal oxides are most effective catalysts for partial oxidation of hydrocarbons. In spite of extensive studies of mechanism and kinetics of these reactions, the main question – which factors determine reaction selectivity – is still under consideration. At the present time role of different surface oxygen species, which are responsible for partial or deep oxidation, are discussed. Oxygen on the oxide surface is known to exist in different states, it differs by coordination environment, binding energy and other properties. For example, there are bridge and terminal oxygen species and hydrated VOH species on the surface of vanadium oxide. Participation of the last species in the partial oxidation is more disputable. All of these species are identified with the use of modern physical methods: NMR, IR, XPS and others. Unfortunately, the potential of these methods for investigations under reaction conditions are strongly limited. For this moment issue on in situ investigations of surface oxygen species, which are responsible for various reaction pathways, is one of the most actual problem in the selective oxidation of hydrocarbons.

In recent years there is appreciable progress in the solving of question on the reaction mechanism, generally due to development of isotopic-kinetic methods, particularly SSITKA technique (Steady-State Isotopic Transient Kinetic Analysis). This technique allows to reveal the main pathways of transformation of labeled reagents into reaction products directly under steady state reaction conditions [1]. In the lecture various methodological aspects of isotopic-kinetic experiments with SSITKA technique as well as mathematical modeling will be discussed. The results of investigation of partial oxidation over widely used vanadia-titania catalysts $(VO_X)_n/TiO_2$ [2] as well as over novel multicomponent oxide catalysts Mo-V-Te-Nb [3] will be presented.

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NMR and EPR spectroscopy in homogeneous catalysis

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The basic principles of electron paramagnetic resonance spectroscopy (EPR) and nuclear magnetic resonance spectroscopy (NMR) are similar. Both methods allow probing with electromagnetic radiation the energy levels emerging in the molecules when they are subjected to an external stationary magnetic field $\vec{B}_0$. In the case of EPR, these levels arise from interaction of $\vec{B}_0$ with magnetic moment of the unpaired electron(s) $\vec{\mu}_e$, in the case of NMR with magnetic moment of nuclei $\vec{\mu}_N$ A magnetic moment ($\vec{\mu}_e$ or $\vec{\mu}_N$) will effectively interact with the oscillating magnetic component $\vec{B}_1$ of electromagnetic radiation if $\Delta E = h\nu$. In this case, the resonant absorption of electromagnetic radiation will occur. The values of ν lie in the radiofrequency range for NMR spectrometers (10-1000 MHz), and in the microwave range 9-10 GHz for the most widely used X-band EPR spectrometers. Only paramagnetic systems can be studied by EPR (organic radicals, certain transition metal complexes, etc), while almost all substances contain magnetic nuclei and are thus accessible to NMR. NMR spectroscopy usually brings most detailed and complete information on the structure of molecules in solution as compared with other spectroscopic methods. Nevertheless, for the studies of the unstable paramagnetic intermediates of the catalytic reactions, EPR spectroscopy can be more appropriate than NMR spectroscopy due to the higher sensitivity, and the absence of the background signals from diamagnetic compounds present in the reaction solution. To illustrate this point the first part of the lecture is devoted to the application of the EPR spectroscopy for the detection and characterization of the active species of the iron catalyzed oxidations. In the second part of the lecture the application of NMR spectroscopy for the studies of the active sites of the catalyst systems for polymerization and oligomerization of α-olefins is considered.

Oxidative dehydrogenation of hydrocarbons on nanostructured catalysts

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Catalytic dehydrogenation reactions used by industry for the production of olefins and styrene are endothermic, their conversion is limited by thermodynamic equilibrium, and they suffer fast deactivation due to coke deposition. Oxidative dehydrogenation (ODH) overcomes these drawbacks, but faces the fast decay of selectivity with increasing conversion, due to overoxidation of the desired product [1]. This limits the product yield and catalyst productivity, which causes that to date its industrial implementation is still an mostly unresolved challenge [2]. Thus, selectivity is the key parameter for reaching practical application.

The intrinsic ODH process complexity and the catalyst multifunctionality imply the need of a close control of many parameters (active centre nature, reactant composition, reaction mechanism, etc.) to improve the selectivity. To get this goal complementary approaches have been proposed: to tune the nature of the active centre, oxidant selection (to avoid overoxidation), and catalyst arrangement [3].

Oxide catalysts play a foremost role in these reactions. At a variance of metal catalysts, their atoms (anions) may take part in the catalytic oxidation reactions. Controlling the properties of oxide catalysts at the nanoscale, by a tailored design of the nanostructure opens new ways to improve the catalytic performance of known catalyst compositions as well as to discover new applicable (i.e., useful) materials and even new functionalities [4,5]. Besides increasing the proportion of atoms accessible to reactants, reduction of particle size down to the nanoscale brings especially a broader range of M-O bond energy values, that may change the reducibility, mobility and electronic character of the oxygen atoms involved, thus bringing unusual selectivity features.

Relevant examples of the unusual performance and the improvement of activity and selectivity attained by nanostructured oxides, such as the high olefin selectivity of oxides known as typical combustion catalysts, will be discussed for several ODH reactions using both conventional (oxygen, air) and unconventional (CO_2) oxidants. These include examples of substituted perovskites, cobalt oxide, and titania and zirconia-based catalysts. Also the new features brought by nanoscale pore diameters in the ordered mesoporous oxides [6] will be discussed in terms of the reaction mechanism and the interaction between homogeneous and heterogeneous processes during the ODH [7].

The proper design and control of the catalyst nanostructure may provide substantial performance improvements. Nevertheless, one must take into account that the working state of the oxide catalyst is either in dynamic equilibrium with or irreversibly modified by the reaction mixture, and the overall process efficiency is highly dependent on reactor and process engineering. As a consequence, further developments towards industrial implementation will need a multidisciplinary approach for the full exploitation of the advantages provided by such a nanostructure control.

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Современное состояние исследований и перспектив развития процесса и катализаторов риформинга бензиновых фракций

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В лекции обобщены результаты исследований состояния платины в алюмоплатиновых катализаторах риформинга (КР), выполненных в ИППУ СО РАН за последние 20 лет. Основным результатом этих исследований является установление важной роли неметаллических состояний платины (Pt^{σ}) в процессах адсорбции и катализе реакций риформинга.

Приводятся результаты исследований состояния активных центров и их свойств в модельных реакций гидрирования бензола, дегидрирования циклогексана, дегидроциклизации гептана, а также в риформинге бензиновых фракций. На основании анализа полученных результатов предложена видоизмененная классическая модель КР, согласно которой на поверхности окиси алюминия присутствуют Pt^{σ}- и Pt^{o}-центры. Такая каталитическая система обладает высокой активностью и способствует протеканию реакции ароматизации с высокой селективностью.

На основании этих данных разработаны варианты оптимальных химических составов и рецептур приготовления новых марок катализаторов для производства ароматических углеводородов (бензола, толуола) и высокооктановых компонентов автобензинов в системах риформинга с неподвижным (экструдаты) и движущимися слоями (сфера) катализаторов.

Сформулированы основные принципы разработки технологий производства высокоэффективных катализаторов и их эксплуатации в промышленных условиях. Освоение производства состояло в разработке, создании и пуске технологий производства носителей (непрерывное осаждение гидроксида алюминия, пластификация и формовка в производстве сферического и экструдированного носителей) и катализаторов (вакуумное увлажнение и циркуляционные схемы пропитки носителей соединениями платины, рения и другими модифицирующими элементами, технологии восстановления, осернения и эксплуатации в рабочих режимах).

Производство экструдированных катализаторов (ПР-71, ПР-81) освоено в промышленном масштабе. Всего выпущено более 500 тонн катализаторов, которые успешно проявили себя при производстве ароматических углеводородов и высокооктановых бензинов на 12 промышленных установках России и Украины. Производство сферических катализаторов освоено в опытно-промышленном масштабе для систем риформинга с неподвижным слоем катализатора (ШПР-81). Первая опытно-промышленная партия катализатора ШПР-81 (22 тонны) наработана в 2011 году и успешно эксплуатируется на установке Л-24-11/600 Омского НПЗ. Приготовление сферического катализатора РДС-С-4 освоено в опытном масштабе (1 кг). Проведены ресурсные испытания в широком диапазоне условий на пилотных установках. Полученные результаты свидетельствуют о его высоких потребительских свойствах, соответствующих современному мировому уровню.

Накопленный более чем 20-летний опыт промышленной эксплуатации катализаторов риформинга ПР-51, ПР-71 и ПР-81, показал, что катализаторы серии ПР проявляют более высокую селективность, чем обычные катализаторы среднеевропейского уровня. Это проявляется в увеличении выхода риформата на 3-5 %мас. с октановым числом ИОЧ = 96-97, повышении (на 3÷5 %) концентрации водорода в циркулирующем газе, снижении содержания бензола и толуола при общем росте содержания ароматических углеводородов [1].

Исследование свойств новых катализаторов позволило открыть принципиально новую возможность их использования в процессах совместной переработки пропан-бутановой и бензиновых фракций в типичные компоненты высокооктановых моторных топлив. Реализацией этой возможности стала разработка трех модификаций новой технологии производства высокооктановых экологически безопасных бензинов с селективностью образования целевого продукта, близкой к 100 %. Важной особенностью новых вариантов технологий риформинга является возможность производства высокооктановых риформатов 4 и 5 класса в соответствии с действующим регламентом моторных топлив. Для этих целей в технологические схемы риформига включены технологические блоки гидроизомеризации бензол- и гептан-содержащих фракций, а также селектокрекинга низкооктановых алканов нормального строения. При этом альтернативной заменой бензолу и толуолу в составе риформинг бензинов выступают экологичные метилциклопентан и его производные [2].

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KEYNOTE LECTURES

Highly active nanocomposite metal-oxide catalysts of low-temperature CO oxidation

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The Pd-ceria based catalysts are the most promising catalysts used for the oxidation of carbon monoxide and other harmful gases for the environment protection.

To improve the efficiency of the catalysts for CO oxidation at low temperatures (room temperature and below) the chemical methods of synthesis (incipient wetness impregnation, coprecipitation, "solution-combustion" etc.) are widely used. The main goal of all methods for the synthesis of low-temperature CO oxidation (LTO CO) catalysts is associated with formation of highly dispersed (up to atomic) state of the active component located at highly defective surface of the support. In this regard, we can note the recent trend in the application of physical methods of synthesis, such as plasma-arc synthesis, microwave discharge, aerosol jet, laser ablation, and others [1-2], which allow obtaining highly dispersed state of the active component, stabilized by highly defective structure of support. In essence, the use of physical methods of synthesis leads to the composite structure of the catalysts, when due to heavy energy impact there is intense sputtering of atoms and clusters of the initial components, followed by the formation of a phase of its own, and mixed interacting phases. Thus, physical methods perform the function of the precursor formation for the composite catalysts, the activation of which is either in an oxygen atmosphere at a calcinations, or due to high temperature hydrothermal treatment.

In this work, in line with global trends for the preparation of composite catalysts for CO oxidation catalysts we examined Pd/CeO_2 and Pd/CeO_2-SnO_2systems prepared by different "chemical" and "physical" methods. The catalysts were prepared, characterized and investigated as series of catalysts with different composition and the preliminary calcination temperature. It was established that the composite catalysts with tin in their composition, prepared under a highly non-equilibrium conditions, both chemical and physical methods, are not only highly active catalysts of LTO CO, but most thermally stable catalysts (up to 1000^{o}C), i.e. pre-heat treatment in an oxygen ambient or in the reaction medium at 1000^{o}C did not affect the following low temperature activity.

The use of complex of structural methods (XRD, HRTEM) and spectral methods (XPS, Raman spectroscopy) has allowed to establish the factors that determine the combination of high activity and thermal stability of the catalysts based on composites Pd/CeO_2-SnO_2, and develop ideas about the microheterogeneity interacting composite catalysts.

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The one-step hydrocracking of vegetable oil over bifunctional catalysts with borate-containing oxide supports

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Hydrocracking of fat and oil raw materials is highly demanding technology of the production of diesel fuels components with improved environmental and operational properties.

The main objectives of this research were studying the effect of the nature of supported components (Pt, Pd, NiO, Co_3O_4, MoO_3, WO_3) and oxide supports (γ-Al_2O_3, ZrO_2, B_2O_3-Al_2O_3, B_2O_3-ZrO_2) on the properties of bifunctional catalysts for hydrocracking of vegetable oil. Optimization of the process parameters and evaluation of the catalytic stability also carried out.

It has been established that catalysts with Pt, Pd, NiO and Co_3O_4 provide complete oil hydrodeoxygenation. Decarboxylation and hydrodecarbonylation are the main reactions for removal of oxygen on Pt and Pd systems. Catalysts with Co_3O_4 and NiO have a high activity in the hydrogenation/dehydration and methanization reactions. Iso-alkanes content in the diesel fraction increases with the growth of the total support acidity.

Owing to the simplicity of preparation of the B_2O_3-Al_2O_3, Pt-containing catalyst on the base of borate-containing alumina was chosen as the most promising for practical application. A scheme of the main transformations of vegetable oil under conditions of the one-step hydrocracking was proposed for this catalyst. That catalytic process takes place at both metal and acid sites over the catalyst. Deactivation during 100 hours time-on-stream of the catalyst could be explained by the decrease of platinum dispersion in hydrothermal conditions and acid sites blockage by polyenic compounds.

Application of conglomerates for separation of the enantiomers

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Production of chiral intermediates required for the synthesis of drugs can be performed by two methods:

1. Separation of enantiomers by selective crystallization with an appropriate enantiomer – resolving agent.
2. Synthesis of enantiomers using chiral catalysts (enzymes, metal complexes with chiral ligands, organocatalysis, etc.)

It should be noted that the optical purity of drugs should generally exceed 99.5% ee.

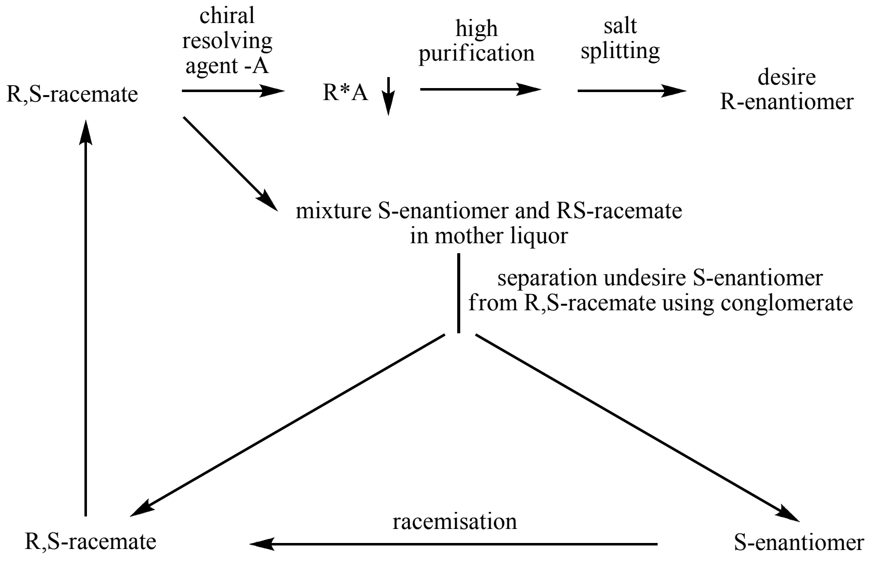
The advantage of the first crystallisation method is the preparation of the desired enantiomer with a high optical purity (> 99.5% ee). A drawback of this method is the low yield (<50%) of the desired enantiomer based on the initial racemate amount.

Use of chiral catalysts for the synthesis of the enantiomers usually leads to an optical purity of 95-99% ee. To obtain the desired optical purity of enantiomer, it is necessary to perform an additional high purification, which makes the process more expensive. To date, the most successful results in the production of enantiomers in terms of price and quality can be achieved using enzymes.

Application of conglomerates for both methods allows achieving a high yield of the desired enantiomer and to obtain the necessary optical purity. The conglomerate is a mechanical mixture of single crystals containing homochiral molecules only1. Conglomerates represent 5 to 10% of the racemic species. In order to find a suitable conglomerate screening of compounds and their derivatives is required.

Scheme 1 shows, that the use of conglomerates and racemization of the undesired S-enantiomer can increase the yield of the desired R-enantiomer to the theoretical ~100% or ~50% without racemization calculated to racemate.

Scheme 1



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The benefits of comprehensive two-dimensional gas-chromatography

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Comprehensive gas chromatography, namely GC×GC, is the last destination reached by separation science. It falls into the category of multidimensional techniques, mainly due to the association of two different mechanisms of separation. Usually on the first column – separation according to boiling points, then on the second column – separation according to polarity.

In fact, comprehensive 2D GC uses the same type of instrumentation utilized in monodimensional GC, but with the novel introduction of the modulator, that places between first and second columns.

There are some kinds of modulators: cryogenic modulators, valve based modulators, thermal modulators.

In general, there are several main advantages of comprehensive GC×GC over conventional 1D GC methods.

First, the selectivity is increased using two separation dimensions of (commonly) volatility, and polarity.

Second, the gain in peak intensity as a result the modulator-driven solute band re-focusing effect causes this technique to be particularly suitable for trace-level component detection.

Third, GC×GC provides highly ordered chromatograms, in which structurally related compounds group together in patterns that facilitates the identification of unknown compounds. Generally, structure-based analyte identification might not necessarily require the resolution of all the constituents of mixtures.

Furthemore, GC×GC allows to decrease separation time owing to use short columns (first and second).

A typical application of GC×GC is presented, along with a consideration of implementation of the GC×GC method

Mechanisms of chemisorption, oxidation and corrosion on platinum metals in oxygen

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Platinum group metals (PGM) are widely used as catalysts in chemical industry and in neutralizers of the automobile exhausts due to their unique properties [1]. It is well known that the chemical composition and structure of a catalyst determine its catalytic activity. During catalytic processes the reaction atmosphere actively interacts with the catalyst. As a result, its structure and composition are changed leading to changes in the catalytic activity. To understand the effect of the oxidative reaction atmosphere on the catalyst structure and composition it is necessary to study the composition and surface microstructure of platinum metals in oxygen atmosphere in the wide temperature and pressure ranges. This communication is devoted to the SEM, EDS and TPD study of the surface microstructure and chemical composition of polycrystalline rhodium, palladium and platinum foils treated in O_2 at 500-1400 K and $Po_2=10^{-5}$-10^5 Pa in order to understand the mechanisms of chemisorption, oxidation and corrosion on platinum metals under these conditions.

The number of oxygen monolayers (*n*) absorbed by Pd(poly) versus exposure to O_2 was derived from our TPD data obtained in the exposure (ε) $=10^{-1}$–10^9 L range at O_2 pressures of 2.6×10^{-6} to 10 Pa and temperatures of 500 and 600 K [2]. The Po_2 ranges were obtained in which the dissociative chemisorption of oxygen on the surface (region A), the insertion of O_{ads} atoms under the surface layer of metal with the formation of a surface oxide (region B), and the dissolution of oxygen in the palladium bulk (region C) mainly take place. The dissociative chemisorption of oxygen on the Pd(poly) surface is observed at low Po_2 values ($\leq 1.3 \times 10^{-5}$ Pa) and $\varepsilon \leq 200$ L. The chemisorbed oxygen coverage of the surface reaches ~0.5 ML (region A). At $Po_2 \geq 10^{-5}$ Pa and $\varepsilon \geq 200$ L, after the saturation of the O_{ads} layer to $\theta \approx 0.5$, O_{ads} atoms begin to insert under the surface layer of the metal (region B). This is a consequence of the decrease in the energy of binding of the chemisorbed oxygen atoms to the palladium surface due to the repulsive interactions between O_{ads} atoms. The insertion of O_{ads} atoms under the surface layer of the metal gradually yields surface palladium oxide, and this accompanied by the absorption of up to ~1 ML of oxygen. The dependence of n on exposure to O_2 demonstrates that, in regions A and B, the curves obtained at 500 and 600 K almost coincide. Therefore, O_2 chemisorption and the formation of the surface oxide on Pd(poly) are almost temperature-independent in this temperature range. At $Po_2 = 0.1$–10.0 Pa and $\varepsilon \geq 10^7$ L, oxygen dissolves in the palladium bulk (region C). The oxygen atoms penetrate deep in the subsurface layers of palladium, diffuse, and accumulate progressively in the metal bulk. Oxygen dissolution in palladium depends strongly on temperature. At $\varepsilon \geq 10^7$ L and $T = 500$ K, palladium absorbs 1–2 ML of oxygen, while at 600 K it absorbs up to ~20 ML of oxygen. A possible reason why oxygen absorption accelerates with an increasing temperature is that the rate of O atom diffusion in the palladium lattice increases. In addition, at $\varepsilon \geq 10^7$ L an increase in the O_2 pressure (≥0.1 Pa) appreciably accelerates oxygen absorption. As the pressure is raised 0.1 to 10 Pa, the amount of oxygen absorbed by polycrystalline palladium at 600 K increases from ~1 to ~20 ML (region C).

This study demonstrated that, at O_2 pressures of 10^{-5} to 10^5 Pa and a temperature of 500 to 1400 K, the interaction between rhodium, palladium, platinum and O_2 includes O_2 chemisorption, oxygen atoms insertion under the surface layer of the metal, the formation of surface oxide film and the diffusion of oxygen atoms into the subsurface layers of metals. An analysis of the dependences of the amount of oxygen absorbed by platinum metals on exposure to O_2, O_2 pressure, and the sample–O_2 contact time revealed the basic regularities in oxygen absorption by the metal under the above-specified conditions and provided a much deeper insight into the causes of the O_2 pressure effect on oxygen dissolution in metals.

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Selective oxidation over gold catalysts

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Supported gold nanoparticles have attracted much attention owing to their unique catalytic properties under mild conditions. In particular, nano-sized gold is well known to display exceptional catalytic performance in low-temperature CO oxidation, water gas shift reaction, propylene epoxidation, hydrogen peroxide synthesis and other important chemical processes. In addition, gold catalysts are increasingly becoming important for the conversion of alcohols and polyols (ethanol, ethyleneglycol, glycerol, sugars, etc.) into valuable products of partial (selective) oxidation. Especially bioethanol is an example of a promising renewable feedstock to obtain corresponding products of oxidation and concurrent reactions: acetaldehyde, 1,1-diethoxyethane, ethyl acetate and acetic acid.

In the present work a set of nanostructured gold catalysts with Au loadings ranging from 0.5 to 7.0 wt% on a TiO_2 support was prepared and evaluated in a gas-phase oxidation of alcohols (EtOH, PrOH, *i*-PrOH, BuOH) and epoxidation of propylene with molecular oxygen, nitrous oxide as well as in the absence of the gas-phase oxidants. The relative contribution of oxidative and non-oxidative dehydrogenation pathways is thus estimated. The presence of oxygen in the feed brought about to a double peak profile of catalytic activity as a function of temperature for oxidation of alcohols. The low-temperature peak fells on 120−130^{o}C. In contrast, the use of N_2O as an oxidant gave rise to usual profile of catalytic activity, which is similar to that of anaerobic dehydrogenation of alcohols. The results obtained allowed to suggest the mechanism of the alcohols oxidation. The low temperature peak is related to participation of active oxygen species, generated from O_2 on the catalyst surface. Oxidation with N_2O is interpreted by preliminary dehydrogenation of alcohols to corresponding carbonyl derivatives followed by H_2 oxidation.

It is known that propylene is able to react with H_2/O_2 mixture over gold particles supported on titania to give selectively propylene oxide. In present work, we disclose that similar epoxidation of propylene can be achieved when CO is applied instead of hydrogen as the reduction agent. The propylene oxide yield goes through the maximum as a function of reaction time, the maximal value being twice higher compared to yield of propylene oxide attained by “traditional” reaction with H_2/O_2 mixture.

SECTION 1:
Fundamentals of catalyst preparation and catalytic processes

Influence of addition of Ag on activity of Pd/SiO_2 catalyst in CO oxidation

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The interest in studies of bimetallic nanoparticles is associated with its unique physical and chemical, structural, electronic, optical and catalytic properties [1]. The structure of the bimetallic nanoparticles is determined by the distribution of metals in it. The particles may be arranged in the form of an alloy having an arbitrary composition or architecture, such as “core-shell”. Improvement of the catalytic properties of bimetallic systems is associated with complex interaction of electrons of two metals and the effects of changes of the lattice parameters in bimetallic alloys or at the interfaces of two metals [2]. Bimetallic Pd-Ag catalysts are interested for hydrogenation reactions [1], oxidation of harmful compound and CO [3]. In some article [4, 5] it was shown that addition of Ag in Pd-containing catalysts leads to formation of Ag-Pd alloy. The decreasing of activity of Ag-Pd catalysts in CO oxidation usually is associated with segregation of silver on the surface of Pd with formation of “core-shell” structure. Segregation of silver takes place at 350 ^oC in red-ox conditions [4]. The increasing of Pd-containing catalysts activity was observed only in case of low loading of silver. That may be associated with formation of Ag clusters on the surface of Pd particles or formation of Ag-Pd alloy concentrated by Pd. The formation of “core-shell” Ag-Pd is not favorable for high activity in CO oxidation.

The aim of this work consists on organization of separated (not alloy, not “core-shell”) but interacted Ag and Pd particles on the surface of support to study role of Ag/Pd interface on the activity in reaction of low-temperature CO oxidation. The silica with wide pores of 20-100 nm was used as support to prevent influence of porosity of support on the size of supported nanoparticles. The series of Ag-Pd/SiO_2 catalysts with different Ag/Pd ratio were prepared. Silica was impregnated by water solution of H_2PdCl_x, and calcined at 500 ^oC for precursor decomposition. Then Pd/SiO_2 materials were impregnated with water solution of $AgNO_3$ and underwent similar thermal treatment. The catalysts were investigated by XRD, UV-vis spectroscopy, TPR H_2, TPR CO and tested in reaction of CO oxidation.

The shift of Pd and Ag reflexes in XRD patterns was observed for bimetallic Ag-Pd/SiO_2 catalysts. That indicated on formation of Ag-Pd interface or formation of two alloys: Pd-milled and Ag-milled. The simultaneous reduction of AgO_x and PdO species in TPR H_2 indicates on formation of Ag/Pd interface. Reduction of oxidized Ag- and Pd-containing species in CO was separately. It indicates on absence of mixed Pd_xAgO_y phases. The shift of PdO reduction in low temperature range in presence of silver confirms contact of Ag- and Pd-containing phases. Pd/SiO_2 catalyst has activity in CO oxidation at temperature above 200 ^oC that may be associated with big size of Pd particles (17 nm according XRD). The increasing of activity was observed for Ag-Pd/SiO_2 catalysts. That may be associated with both decreasing of Pd particles size (according XRD) and presence of Ag/Pd interface which is favourable for oxidation of CO. We suggest that activation of molecular oxygen occurs on the surface of silver particles. Activation of CO takes place on Pd-containing species. Thus, CO oxidation may occur on the Ag-Pd interface due to spillover of CO from Pd particle and atomic oxygen from silver.

The design of bimetallic catalysts with separated but interacted Ag and Pd particles may be prospective way for development of high effective catalysts for oxidation of harmful organic compound and CO.

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Synthesis of Fe@C-Pd hybrid nanomaterials and investigation their catalytic activity in Heck coupling reactions

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Synthesis of inorganic hybrid nanostructures based on ferromagnetic materials is one of the rapidly developing areas in nanomaterial chemistry. Recently, there has been a widespread trend concerning synthesis of iron-palladium nanoparticles for new magnetically controlled catalytic systems for the reactions of new C-C bond formation [1]. Most of the works on this subject include a chemical synthesis of hybrid nanomaterial using sonochemical reactions method [2], or via ion-exchange reactions on the surface of iron nanoparticles [3], wherein the obtained hybrid nanomaterials have active centers of two metals on its surface. Therefore, the most relevant in this framework is the creation of the materials using magnetic metal oxide nanoparticles coated with a carbon shell, what let us get only the active centers of palladium on the surface and prevent degradation of the catalyst in the reaction mixture [4,5].

We proposed a method for producing nanoparticles Fe@C-Pd, based on the sorption of Pd^{2+} on the iron nanoparticles surface coated with carbon with its further reduction by $NaBH_4$. The nanoparticles were obtained by electro-spark dispersing of metallic granules in hexane. [6] The resulting nanoparticles were analyzed by XRD, which showed the appearance of bands at 2θ equal to 40, 47, 68, corresponding to Pd^0, and confirms the successful modification of nanoparticles.

Also as part of the work the kinetics of the palladium sorption on the nanoparticles surface was investigated. It has been shown that the process is reversible, and relates to the first-order reactions. Langmuir type of adsorption isotherm of the process confirmed the formation of a monomolecular layer of palladium ions on the surface of the nanoparticles. The limit adsorption, which is amounted to $7{,}34 \cdot 10^{-7}$ mol / g, and Henry constant $1{,}16 \cdot 10^{8}$ l / mol, indicating the formation of strong binding between the palladium ions and nanoparticles surface.

The catalytic activity of the obtained nanoparticles was studied in the reaction of new C-C bonds formation, for example, Heck reaction [4]. The reaction was carried out with iodobenzene derivatives and styrene, in DMF with the reflux of the reaction mixture. Triethylamine was used as a base, the amount of inserted of the catalyst was 40 mg.

It has been shown that using Fe@C-Pd nanoparticles as the catalyst promotes the production of various trans-stilbene derivatives which contain various substituents in p-position of the benzene ring with the product yields verifying from satisfying to high. Furthermore, the possibility of reusing the catalyst into the similar conversion with slightly changes in the yield of desired products is proved.

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Low-temperature CO oxidation over silica-supported Ag catalysts

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Nanosized Ag catalysts attract much attention due to their unique catalytic properties in various reactions, in particular, in CO oxidation at low temperatures. Recently, Ag/SiO_2 catalysts showing high catalytic activity in CO oxidation and reaction stability at ambient temperatures have been described in literature [1, 2]. However, the nature of active species as well as effect of hydroxyl coverage of silica on the surface properties of Ag/SiO_2 catalysts was not thoroughly investigated. The purpose of the present research work is to study the influence of pretreatment temperature of silica on the surface properties and catalytic activity of Ag/SiO_2 catalysts.

The Ag/SiO_2 catalysts were prepared by the wetness impregnation method using $AgNO_3$ as precursor followed by oxidative treatment in air flow at 500 ^oC and reduction in H_2 flow at 200 ^oC. Loading of silver was 5 % wt. Catalysts were characterized by TPR-H_2, TPD-O_2, TPSR-CO, XRD, TEM, UV-visible DR spectroscopy and N_2 adsorption at -196 ^oC. Quantity of OH-group on the silica surface was estimated by means of TPD-H_2O method. Catalysts were tested in a flow fixed-bed reactor at atmospheric pressure using 0.1 g of catalyst and gas mixture, containing 1%CO+1%O_2 in He (20 ml/min).

Comparison of Ag/SiO_2 catalysts prepared on the basis of silica preliminary calcined at 500, 700 and 900 ^oC was carried out. It was stated that OH-groups of silica surface are able to stabilize highly dispersed AgO_x ($x<0.5$) species (in particular, clusters of silver oxide), which are formed in the course of the oxidative treatment. The agglomeration of highly dispersed AgO_x species into defective Ag_2O particles occurs when the ratio between amount of OH-groups (normalized on support mass) and silver (OH/Ag ratio) in the prepared catalyst decreases. Both decreasing of the surface area and increasing of silver loading facilitates the agglomeration of highly dispersed AgO_x species. Thus, the formation of Ag_2O particles with sizes of 7.0 and 11.3 nm for Ag/SiO_2-700 and Ag/SiO_2-900, respectively, were observed after oxidative treatment.

Subsequent reduction of Ag/SiO_2 samples results in formation of metallic Ag nanoparticles, which are able to adsorb oxygen at 25 ^oC. However, the nature and amount of adsorbed species is different for Ag/SiO_2-500, Ag/SiO_2-700 and Ag/SiO_2-900 catalysts due to different structure and dispersion of Ag particles. Reduction of defective Ag_2O particles formed on the surface of Ag/SiO_2-700 and Ag/SiO_2-900 samples results in formation of defective Ag particles, consisting of several crystal domains. The nature of oxygen species adsorbed on the interdomain boundaries is probably an ionic one. This provides an additional delocalization of electron density with formation of $Ag^{\delta+}$ sites. Adsorption and activation of CO molecules occurs with participation of these sites. Oxygen adsorbed on the surface of Ag/SiO_2-500 catalyst is less ionic in its nature, and formation of $Ag^{\delta+}$ sites, required for CO adsorption, does not take place. The Ag/SiO_2-700 catalyst demonstrates the highest low-temperature activity in CO oxidation among all samples investigated. Decreasing of catalytic activity for Ag/SiO_2-900 catalyst is connected with low specific surface area of SiO_2-900 sample and, as a consequence, low dispersion of Ag particles.

In addition, it was shown that the presence of water vapor (corresponding to ambient humidity, RH=50-70%) in reaction mixture influences on the catalytic activity negatively. It may be associated with water adsorption on active sites.

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Synthesis of F-doped TiO_2 powders via "reverse" hydrolysis of titanium tetraisopropoxide for photocatalytic processes

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Titanium dioxide is widely used in photocatalysis due to its high activity and chemical stability in such processes. Structure of the obtained material is significantly affect the photocatalytic properties of TiO_2 powders. Over the past decades interest in obtaining and studying nanoscale mesoporous TiO_2 powders with a large specific surface area has increased. Therefore control of the particle size distribution, morphology, porosity, phase composition is important factors in properties control of the final material [1]. There are many methods for the synthesis superfine titanium dioxide powders [2], however, hydrolysis of titanium alkoxides is one of the simplest methods of its obtaining [3].

In this work F-TiO_2 was obtained through hydrolyses of titanium tetraisopropoxide in the presence of NH_4F. However, in the course of hydrolysis the alkoxides usually added to the excess of hydrolytic reagent, yet in this research work the order of mixing was reversed. Structural features, phase composition, specific surface area were studied by: transmission electron microscopy (TEM), BET, X-ray analysis (XRD), respectively. It was found that hydrolysis of titanium tetraisopropoxide in the presence of NH_4F during the reverse mixing leads to the formation of titanium dioxide powder with superfine morphology and particle size about 40 nm. F-TiO_2 has a middle specific surface area and presence of fluoride in structure influences porosity. Samples containing fluorine have bigger porosity values than bare TiO_2 powder prepare in presence of H_2O by same method. Probably porosity and pore size increasing relates the presence of ammonium fluoride when high porous sol is formed, which after heat treatment retains the structure. According to XRD data fluorine content has a big influence on the TiO_2 structure as it makes the amount of anatase increase, prevents thermal transition of anatase into rutile and significantly improves titanium dioxide photocatalystic activity.

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Pd-Ni/CeO_2 catalysts for low-temperature CO oxidation

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The reaction inhibition effect in CO oxidation at low temperatures occurs on palladium-based catalysts which representing Pd^0/PdO nanoparticles on conventional supports, like Al_2O_3, SiO_2. This effect leads to suppress $CO+O_2$ reaction at temperatures below 150°C. Investigation of Pd/RO (RO-reducible oxides) catalysts is of a great interest because of these catalysts are not affected by CO poison which leads to effective catalysis of CO oxidation below 0°C. Pd/CeO_2 catalysts are one of the most investigated systems due to combination of properties: high activity, thermal stability, low influence of impurities, etc. Earlier we showed that no Pd^0/PdO nanoparticles are formed in Pd/CeO_2 catalysts in comparison with Pd/Al_2O_3 one, and strong interaction of ionic palladium with support with formation of solid solutions $Pd_xCe_{1-x}O_2$ is realized [1,2]. This fundamental difference in the chemistry of these catalysts from traditional Pd/Al_2O_3 catalysts is definitely bound with the formation of the active centers of different structure and properties, and there is no generally accepted opinion about these structures and its properties in scientific community at this moment.

Solid solution $Pd_xCe_{1-x}O_{2-x-d}$ structure was investigated by a complex of the physical methods (XRD, PDF, XPS, Raman spectroscopy) in combination with the DFT calculations using Pd/CeO_2 catalysts with high Pd loading obtained by coprecipitation [3]. It was shown that palladium ions, replacing $Ce^{3/4+}$ ions in ceria fluorite structure, retain a divalent state and a square-planar environment due to the shift from cationic fluorite position. The resulting structures are stabilized by a water molecules in its dissociated state as OH^- groups in the anionic fluorite positions. Formation of these structures leads to two positive effects: oxygen vacancy formation energy in the lattice of $Pd_xCe_{1-x}O_{2-x-d}$ is strongly decreased, and a thermal stabilization effect of dispersed particles is observed. Thus, the introduction of palladium into ceria lattice results in substantial increase of thermal stability of these catalysts with preservation of high activity in $CO + O_2$ reaction at low temperatures.

Application of DFT calculations allowed to demonstrate that nickel, which is palladium electronic analogue, is also capable for incorporation into the fluorite structure with formation of solid solutions $Ni_xCe_{1-x}O_{2-x-d}$ of the similar structure. On the base of these data the successful attempt to replace some part of palladium by a nickel in the fluorite lattice was made. It was shown the obtained PdNi/CeO_2 catalysts are active in $CO+O_2$ reaction at 0°C after calcination even at 900°C.

Presentation will focus on the promoting effect of nickel, and the structure and properties of solid solution $Pd_xCe_{1-x}O_{2-x-d}$ will be discussed in detail.

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Effect of dopant on structure and phase composition of MoVTeNbO catalysts for selective oxidation of C2-C3 alkanes

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MoVTeNb oxide catalysts are promising systems for selective transformations of C_2-C_3 alkanes. The main components of these catalysts are orthorhombic M1 and pseudohexagonal M2 phases [1]. In this decade, research efforts continue to focus on finding effective promoters in primary four component MoVTeNbO composition for increasing the efficiency of the catalysts. HRTEM methods were used for investigation of MoVTeNbO catalysts promoted by bismuth, calcium, zirconium, etc.

The study of the morphology, crystalline structure and the phase composition was carried out using a JEM-2010 microscope (the accelerating voltage - 200 kV; the lattice resolution - 1.4 Å). Local elemental analysis was performed by EDX method (Phoenix Spectrometer with Si(Li) detector; an energy resolution is about 130 eV). Samples for the HRTEM measurements were prepared by ultrasonic dispergation a small quantity of the powder for a few minutes in ethanol onto standard carboncoated copper grids. Simulation of crystal structures and TEM images was performed using the multislice method of calculation wave function by complex programs “Musli” (developed BIC) [2]. The Rietveld method and known structural information were used for quantitative phase analysis by XRD.

Promotion of the catalyst leads to a change in the phase composition and catalytic properties in reactions of propane ammoxidation and ethane oxidative dehydrogenation according to the type and content of the dopants. The formation of crystalline structures phases M1 and M2 in the modified samples occurs through the formation of nanostructured precursors from amorphized particles with approximate of the cationic composition to the final phases. Thus, bismuth may be included in phases M1, however other promoters constitute the individual oxide phases.

Electron microscopic studies confirm the occurrence of Bi in the structure of M1 phase. This is accompanied by disorientation along the [001] direction (perpendicular to the image plane) in phase M1, which is manifested in the images distortion (210) plane at an angle of about 5˚.

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Model catalytic systems prepared by RF-plasma sputtering technique

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Metal nanoparticles are widely used as active components of catalysts nowadays. The nature of metal states active in different reactions and the detailed mechanism of their catalytic action are of particular interest. The study of real catalysts is a complicated task as one should keep in mind lots of different factors: inhomogeneous distribution of active components, interaction with supports, possible influence of impurities etc. Therefore the model catalysts are ideal systems for establishing fundamental aspects of catalytic action. The metal nanoparticles deposited on a flat surface of supports are usually used as convenient model samples for the investigation by different physical methods.

In our work we applied the RF-discharge for sputtering of the metal's electrode in an inert or oxygen atmosphere to produce metallic or oxidized species deposited on a support. The technique allows to obtain nanoparticles with a narrow size distribution at room temperature. All experiments were carried out in chambers of photoelectron spectrometer VG ESCALAB HP without direct contact of samples with ambient. The prepared nanoparticles were analyzed by X-ray photoelectron spectroscopy (XPS), temperature programmed desorption (TPD) and their catalytic activity in CO oxidation was tested. The particles size was determined by transmission electron microscopy (TEM). Oxidized tantalum foil and carbon film were used as supports.

The nanoparticles of palladium, platinum, silver and gold were analyzed. For all metals the RF-sputtering in an oxygen atmosphere led to the formation of highly oxidized species: Pd^{4+}, Pt^{4+}, Ag^{3+} and Au^{3+}. The analysis of metal's and oxygen states in the obtained nanoparticles was performed using Pd3d, Pt4f, Ag3d, Au4f and O1s spectra.

The high resolution transmission electron microscopy data showed that the synthesized nanoparticles comprised numerous extended defects of intergrain boundaries type. For gold and silver the nanoparticles mostly tended to have a symmetric spherical shape. In case of palladium the extensive islands of irregular shape were observed.

The thermal stability of all highly oxidized species did not exceed 373-423 K. The reaction probability towards CO oxidation was analyzed for all obtained oxidized nanoparticles. The highly oxidized species showed the highest reaction probability. The CO exposure at room temperatures led to the reduction of these species. In case of palladium and platinum the reduction proceeded through the formation of Me(2+) species (Pd^{2+}, Pt^{2+}) followed by the reduction to the metallic state. The highly oxidized silver nanoparticles interacted with CO with a high reaction probability through $Ag^{3+} \rightarrow Ag^{1+} \rightarrow Ag^{0}$ states, whereas the formation of the possible intermediate Au(1+) species was not detected during CO exposure to AuOx nanoparticles.

The RF-sputtering in an argon atmosphere led to the formation of metallic nanoparticles with a narrow size distribution. The palladium nanoparticles were deposited on carbon films and nitrogen-modified carbon films. It was shown that the spectral characteristics of the prepared model systems and real catalysts based on Pd supported on N-modified carbon nanofibers are in good agreement. The dependence of palladium states on the defects and N,O –containing groups on the surface of carbon films was discussed.

The obtained results showed that the RF-sputtering technique can be an efficient tool for synthesis of model catalytic systems that can be easily studied by physicochemical methods and used for the analysis of the properties of real catalysts.

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Quantum chemical study of some metal oxide structures and their interaction with CO

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The oxides of transition metals are widely used as efficient catalysts in many technological processes. At that, multicomponent metal oxide systems exhibit higher activity and selectivity in comparison with the catalysts containing only one of the components, in particular, in the conversion of CO to CO_2. In order to study the features of such activity we performed quantum–chemical calculations of various metal oxide systems (presented below) using Gamess US program [1]. The calculations have been carried out in cluster approach using DFT/B3LYP with split-valence basis sets.

First of all clusters of aluminum $(Al_2O_3)_n$, n = 1 – 8 and copper $(CuO)_m$, m = 1 – 4, 6, 8, 16 oxides have been studied. Features of their geometric, electronic structure, charge and energy characteristics have been determined. To find the most stable oxide clusters, corresponding to the energy minima, the possible spin states were taken into account in the calculations and clusters with different multiplicity were considered. To evaluate the stability of the aluminum and copper oxide clusters the binding and atomization energies were calculated.

In the continuation, the features of the interaction with CO of formed aluminum and copper oxide clusters were studied. To determine the optimum conditions for CO interaction with clusters, we observed various potential active centers and various positions of CO while C=O distance was fixed.

The calculations of copper-aluminum oxide clusters obtained by the substitution of the part of aluminum oxide cluster to the copper one allowed to propose structures suitable for modeling the respective metal-oxide systems and CO adsorption on them. The comparison of the results obtained for the aluminum and copper oxide clusters with the results obtained for the combined copper-aluminum oxide clusters will be useful in understanding the catalytic activity of multicomponent metal oxide systems.

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Study of the composition and morphology of titanium-magnesium catalysts for ethylene polymerization

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The major part of the total high-density polyethylene is produced with the use of supported Ziegler-type titanium-magnesium catalysts (TMCs) ($TiCl_4/MgCl_2 + AlR_3$). New modifications of the catalysts are studied and designed to improve the process of ethylene polymerization, to expand brand assortment and to enhance the polymer quality. Parameters of the catalysts (chemical and phase composition, morphology, pore structure, particle size and particle size distribution) play a key role in the design of polymerization process and influence the technological properties of polymer powder produced during polymerization. Determination of relationships between textural properties of supported catalysts, polymerization conditions and morphology of the polymers produced makes it possible to optimize the production of catalyst and polymer particles with desired properties.

In the recent work, titanium-magnesium catalysts with various composition and morphology, prepared with different $MgCl_2$-containing supports, were studied. Chemical composition of the supports and TMCs was studied by atomic emission spectrometry, ^{13}C NMR and ^{1}H NMR spectroscopy, chromatography, etc. According to ^{1}H NMR spectrometry, new catalyst modifications with the supports obtained by the interaction of solutions of organomagnesium compound $Ph_4Mg_3Cl_2$ and silane compounds $SiR_xCl_y(OEt)_z$ comprise the OEt groups (8-17 wt.%). Treatment of the supports with $TiCl_4$ and activation of the catalysts by organoaluminum compounds did not remove the OEt groups from the initial compounds. ^{13}C NMR spectroscopy of their solutions in tetrahydrofuran showed that some part of OEt groups in new modifications of the supports was in form of EtOH. Phase composition and morphology of the supports and catalysts were studied by X-ray analysis, low temperature nitrogen adsorption, laser light scattering and scanning electron microscopy. The X-ray study of the supports and catalysts revealed that their new modifications have a more disordered crystal structure. X-ray patterns of the new catalysts and supports have peaks typical of the $MgCl_2 \cdot nEtOH$ adducts [1-3]. The low temperature nitrogen adsorption measurements demonstrated that the pore structure of TMCs modified by OEt groups evolves after their treatment with organoaluminum compounds. Among the synthesized catalysts under consideration, new modifications of TMCs activated by organoaluminum compounds have the highest specific surface area (350–500 m^2/g) and a small pore diameter (≈ 3 nm). As shown by laser light scattering (MALVERN) and scanning electron microscopy, the catalyst particles have uniform shape and narrow particle size distribution.

TMCs synthesized with different compounds and having different textural properties were tested in ethylene polymerization. The catalytic activity, the ability of the catalysts to control the flow melt index (molecular weight) by hydrogen, and morphology of the polymers obtained were studied. New catalyst modifications better control the molecular weight of polyethylene by hydrogen. Polymers obtained on these catalysts have high bulk density and narrow particle size distribution. High specific surface area and small pore diameter of the catalysts were shown to produce a higher bulk density of the polymers.

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In situ study of active component of catalyst during MWCNT growth

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Multi-walled carbon nanotubes (MWCNTs) are known to be perspective component for numerical composite materials due to their unique mechanical properties and high thermal and electrical conductivity [1–3]. Their properties mainly depend on the diameter distribution and defect concentration, which, in turn, depend on the catalyst nature and growth conditions. Previously it was demonstrated that the formation of the catalytic species and nucleation of the carbon deposits determine the selectivity and activity of nanotube growth process [4]. Thus, the investigation of the catalyst active component formation and carbon nucleation is extremely important for the design of selective processes of MWCNT production [5-6]. In the present work the formation of the active component of the bimetallic Fe-Co catalyst during MWCNT growth was studied using *in situ* and *ex situ* synchrotron radiation X-ray diffraction analysis (SRXRD). The XRD data in combination with the results of other physical methods (*ex situ* high-resolution transmission electron microscopy (HRTEM), internal field ^{59}Co nuclear magnetic resonance (NMR), gas chromatography) can be used for the development of kinetic model and the optimization of the synthesis conditions to produce MWCNT with controlled properties in a fluidized bed reactor.

Detailed kinetic study of the nanotube growth allowed observing the induction period characterized by the absence of intensive MWCNT growth. According to *in situ* SRXRD data at least four processes can be distinguished during the induction period, such as active metal reduction, metal particles growth and/or agglomeration, their saturation with carbon and MWCNT nucleation. These processes follow each other, except the second and the third one which occur simultaneously.

For the first time we have obtained data confirming the stepwise formation of Fe-Co bimetallic alloy. It was found that the cobalt particles are formed at the first stage of catalyst reduction. These primary particles promote the reduction of Fe species with the subsequent formation of the alloy. Mono-component Fe catalyst demonstrates the simultaneous formation of Fe–C alloys (austenite and tetragonal ferrite-like structure) with subsequent transformation into stable iron carbide Fe_3C (cohenite). The *in situ* activation of the bimetal Fe–Co catalysts supported on Al-based oxides and CaO leads to the formation of highly dispersed alloyed particles with bcc structure type. Meanwhile, the stable carbide formation for such systems is not observed. The absence of stable carbides promotes effective carbon diffusion through metal particle providing much higher activity of multicomponent Fe–Co catalysts compared to that of monometal Fe catalysts. According to the XRD data, catalyst active component (alloyed metal particles) is solid or at least contains crystalline core during CNT growth. Kinetic model of active component formation was developed. This model is in good agreement with obtained experimental data. Pechini-type method of Fe–Co catalyst production demonstrates much higher MWNT production with different structural properties than it was described before [7,8].

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Investigation of the mechanism of catalytic reactions with use a stable isotopes

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The development of oil refining processes promotes to produce the high quality fuel with improved properties. At the same time, technology modernization is impossible without fundamental research of the reaction mechanism. This is the aim of this work. The study of the stages and directions of the catalytic reactions is possible using reagents with labeled atoms. The method of isotope ratio mass spectrometry (IRMS) is investigated of the reactions joint transformation of hydrocarbons on the different catalytic systems.

The hydrogen transfer reactions between the hydrocarbons (the donors and acceptors of the hydrogen) were carried out on the zeolite catalysts in the conditions of cracking. The cyclohexane-H_{12} and cyclohexane-D_{12} – hydrogen donors, 1-hexene and 2-methylthiophene – hydrogen acceptors were used as reagents.

The catalytic experiments were carried out on aluminaplatinum catalysts in the conditions of catalytic reforming to establish the possibility of involvement of light hydrocarbon gases in joint transformation with C_{5+} hydrocarbons. The n-butane (with labeled carbon atom $^{13}CH_3$-C_3H_7) and n-hexane were used as model mixture.

The quantitative analysis of the stable isotopes of hydrogen (D и H) and carbon (^{13}C и ^{12}C) in the reagents and products was determined by method IRMS. The experiments were carried out on the isotopic mass spectrometer *DELTA V Advantage* (“Thermo Fisher Scientific”) in the configuration with gas chromatograph via pyrolysis or combustion reactor and with an interface *ConFlo IV* for online continuous flow of carrier gas helium. The individual conditions of chromatographic separation of the components were choose for each reaction. The isotopic composition of elements (δ, ‰) was calculated relative to the international standard VSMOW for hydrogen, and VPDB for carbon.

According to the isotope analysis the high content of deuterium in the pentanes and hexanes was ascertained as are the main products of the reaction of hydrogen transfer. This allowed to assume the directions of the hydrogen transfer mechanism between donors and acceptors of hydrogen.

The results of IRMS analysis confirm the coupling effect in the transformation of n-butane with C_{5+} hydrocarbons, that shows the actual possibility of joint processing of hydrocarbon gases with a gasoline fractions.

The use of reagents with labeled stable isotopes allowed to establish the main stages and directions of transformation hydrocarbons with a different catalysts and conditions. Thereby, the catalytic reactions were investigated by the method IRMS and the optimal conditions of processing were selected to produce of high quality fuel.

The effect of Cr/Fe ratio on the structural features of Fe-Cr-Cu-containing oxide catalysts

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The mixed Cu-Fe-Cr oxides attract great attention because of their magnetic features as well as various oxidation-reduction and catalytic properties [1, 2]. In the present work, structural features of the mixed $Cu(Fe_xCr_{1-x})_2O_4$ spinels, serving as the catalysts for water gas shift reaction, were investigated. Samples of the $Cu(Fe_xCr_{1-x})_2$ cationic composition (where x = 0, 0.25, 0.5 and 0.75) were obtained by a co-precipitation method from the nitrate solutions of the corresponding metals with sodium carbonate or ammonium solution and calcined in air at a temperature higher than that of spinels crystallization [3]. The structure of the resulting phases was studied using the methods of thermal analysis, ex- and in-situ powder diffraction, high resolution electron microscopy, IR spectroscopy, Ultraviolet-Visible-Near Infrared Diffuse Reflectance Spectroscopy (UV-Vis-NIR DRS) and EXAFS spectroscopy.

Variation of a Fe/Cr ratio was shown to change the degree of tetragonal distortion of the spinel structure from 1.06 to 0.95. At Fe/Cr = 1 the spinel becomes cubic. A crystallographic relation between cubic spinel structure (Fd3m) lattice parameters and those of tetragonally distorted one ($F4_1\backslash ddm$) was considered. The cationic distribution of copper ions in the studied spinels was analyzed using the energy of preference and the chemical composition. The data obtained were verified experimentally by spectral methods. A correlation of copper distribution over tetrahedral and octahedral positions with the catalytic properties in low-temperature water gas shift reaction was revealed.

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Physicochemical properties of ultrafine powders prepared by laser ablation of crystalline silicon in water

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Silicon based materials are one of the most intensively studied since they are widely used in different fields of science and technology. It is necessary to mark out a laser ablation method among numerous methods for preparation of silicon contained materials. It allows to obtain nanoparticles dispersions of wide range of materials, such as oxides, hydroxides, carbonates as well composites with more difficult composition, including core@shell structures. An important feature of nanoparticles obtained by high energy laser ablation is its defect structure, leading to appearance of new optical, antibacterial and catalytic properties.

In this work silicon based dispersions were obtained by laser ablation of single-crystal silicon target in liquid. Dried powders were heat treated at 200, 550, 700, 900 and 1000 °C in air for 12 hours as well at 1000 °C in argon.

It was shown that particles obtained by laser ablation of silicon target in water contain amorphous or crystalline silicon core and silica shell obtained during ablation by reaction with water contained dissolved oxygen.

Changes research, taking place at heat treatment of air dried powders, shown that it ascribe to disappearance of crystalline silicon reflection at diffraction pattern caused presumably by its oxidation. At the same time, O/Si ratio decreases according to IR spectroscopy. Such features are observed at annealing of sample both in air and in argon and can be explained by behavior of followed reaction: $Si + SiO_2 \rightarrow 2SiO$ [1]. Assumptions about reaction of silicon with its oxide and oxygen deficient centers forming are confirmed by research of absorbance and fluorescence spectra of powders. Band with maximum at 330-370 nm region corresponds to bulk oxygen deficient centers incorporated in rings [2] and band at 420 nm can be attributed to surface dioxasilirane groups. According to XPS data, oxygen defects, which appear at annealing, are bulk defects and absence on the surface that confirms an interpretation of absorbance spectra.

Thus, heat treatment of silicon contained nanoparticles obtained by laser ablation favours the appearance of oxygen vacancies that makes application of such materials perspective for catalysis, sensors and optics.

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Selective hydrogenation of acetylene: influence of palladium precursor on adsorption characteristics of supported metal particles

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In present day a rather strict requirements for the content of acetylene in ethylene product, which is used for preparation of polymeric materials. Purification of these impurities from the ethylene by selective hydrogenation is carried out generally in the presence of alumina-supported palladium catalysts [1-2]. The disadvantages of traditional alumina-supported palladium catalysts hydrogenation of acetylene in ethane-ethylene fraction is: oligomerization of unsaturated hydrocarbon molecules on acid sites of support, which lead to accumulation of condensation products on the catalyst surface, and cause them to accelerated deactivation; side reactions of hydrogenation of acetylene to ethylene and ethane on palladium particles with deficiency of electron which leads to lower yield of ethylene. Solution for the first disadvantage of these catalysts was carried out in our earlier papers by optimizing the acidic properties of the carrier by changing its phase composition during heat treatment of the parent compound - γ-alumina modified to give δ-Al_2O_3.

A second drawback of these catalysts associated electronic state of palladium particles due to the manifestation of two factors: the size effect and the effect of a strong metal-support interaction. The first is the change in the electron configuration of palladium atoms by varying the diameter (dispersion) supported metal particles, the second - with the interaction of palladium particles with surface acid-base centers with the manifestation of the donor-acceptor interaction. Thus for alumina supported palladium systems dimensional effect is prevailing, which can be varied by changing the nature of the source of palladium precursor.

The aim of this work was to study the influence of the nature of the precursor of palladium on electronic and geometric characteristics of the supported palladium particles and their adsorption properties in the selective hydrogenation of acetylene.

It has been established that dispersion of palladium catalysts synthesized using the acetylacetonate precursor (D = 39.5 %), is 1.4 times more as compared with the acetate samples (D = 30.6 %), due to the smaller 1.3 times the average diameter (2.8 nm) was formed palladium particles on support surface. It was determined that the surface atoms of Pd catalyst synthesized by applying $Pd(AcAc)_2$, are less electron density on the valence orbitals compared to acetate samples that caused the higher coordination unsaturated palladium particles, leading to a reduction in the collective properties of the electronic structure of atoms in the metallic palladium particles. These catalytic tests indicate that the conversion of acetylene depends on the dispersion of supported palladium particles for samples synthesized using acetylacetonate complex is higher than for acetate catalysts that is caused by higher degree of dispersion of the first metal samples. The selectivity of conversion of acetylene to ethylene is determined by valence state electronic orbitals of the surface atoms of palladium acetate and 1.3 times in systems greater than acetylacetonate catalysts characterized by a high electron density on the valence orbitals.

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Kinetics study of the tetrachloroethylene hydrofluorination into pentafluoroethane over a Cr-Mg catalyst

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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, in particular, chromium–magnesium catalysts [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) [3]. The catalyst is finally formed under the action of fluorine containing mixtures under conditions of a catalytic reaction or fluorinating preactivation.

In this work, we studied the influence of the heat treatment conditions (temperature and gas phase composition) on the physicochemical and catalytic properties of chromium–magnesium catalysts and kinetic study on the most active sample.

The precursor of catalysts samples was prepared by impregnation of powder magnesium fluoride with aqueous solution of $CrCl_3$. The BET specific surface area was equal to 50-60 $m^2\ g^{-1}$. The catalyst contained 12 wt.% of chromium chloride. 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 was shown that by changing the activation conditions can form the catalysts with very different catalytic properties for the same initial catalytic system. More efficient way of enhancing the catalytic activity procedure involving heat treatment in air.

Kinetic regularities of the vapor-phase hydrofluorination of perchloroethylene were studied at the total pressure of 0.4 MPa, temperature 300–380^{o}C, contact time 0.5–5 s and the molar ratio HF:PCE = 10. The experimental setup included a reactor placed into a heat chamber, which permitted one to vary the temperature of the reactor from 300 to 380°C. The reactor was built as a U-type nickel tube (i.d. 0.6 cm, volume 6 cm^3). The concentration of PCE in HF was set via saturation of the gaseous hydrogen fluoride flow with the perchloroethylene vapors in an evaporator. The gaseous product mixture was passed through a scrubber with dry alkaline metal carbonate, in which HF and HCl were converted into CO_2 and H_2O, and then was analyzed by chromatography on-line.

The overall process includes a large number of possible reaction routes and, apart from its main products, might yield the products of side reactions like isomerization, elimination and disproportionation [4]. Based on the experimental data, the pathway of perchloroethylene fluorination with HF was identified. The process involves several consecutive reactions for the formation of main fluorination products and parallel reactions for the formation of by-products. The rate constants and activation energy of the PCE conversion was obtained on the assumption of the first order of the reaction rate.

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Activation of Ni-containing NASICON catalysts of isobutanol dehydration by plasma chemical treatment

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Plasma–chemical treatment allows to obtain completely new materials with widely varied surface properties, while preserving most properties of the original materials. This advantage is used in the activation of catalysts and adsorbents. In some cases, plasma–chemical treatment (PCT) leads to a multifold increase in the activity of catalysts, due to changes in the nature of their active sites [1–2].

Framework zirconium phosphates of the NASICON (NZP) type with the basic composition $NaZr_2(PO_4)_3$ are attracting increasing attention of specialists in the field of catalysis. The basic structure of double sodium–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 [3–4].

The NZP (Na-Zr-phosphate) is of NASICON type in which nickel and cobalt as ions-modifier replaces a sodium ion in a cationic part of crystalline structure. The influence of such chemical modification and of pretreatment of NZP-catalysts in glow-discharge Ar and H_2 plasma on its activity and selectivity was studied as the object of research. Obtained in paralleled reactions dehydration-dehydrogenation the products of isobutanol's transformations are influenced by specified ions and its new states after plasma activation. The acidity of the catalysts was determined by studying the adsorption of pyridine from nonaqueous solutions by means of UV-spectra of test-molecule. Adsorption of CO_2 was studied.

It was shown that the character of activation did not depend on the selection of the plasma-forming gas (Ar or H_2). Surface modification by plasma treatments create new adsorption sites with differences by the thermodynamic characteristics of CO_2 and the polarization of the adsorbate molecules. After the plasma chemical treatment in Ar and H_2 the butanol convesion increases in 2–3 times; selectivity of dehydration decreases by 10–15%, yield of keton grows due to the increase of general conversion of alcohol. After the plasma treatments the values of E_a^{BUT} increases, it can be explained by the decrease of strength of alcohol bonds with the surface that promotes butanes formation. A similar value of E_a^{BUT} after the both plasma treatments testifies to an invariance of the nature of the dehydration centers. We are led to conclude that the surface state after plasma treatment in Ar is unstable and changes during catalytic experiments. Reactivity changes and the number of dehydration centers increases under the action of the reaction medium, whereas dehydrogenation centers return to their initial state.

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First example of continuous-flow selective hydrogenation of functionalized nitrobenzenes to anilines over gold nanoparticles supported on alumina

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Functionalized anilines are an important class of industrial intermediates for a variety of specific and fine chemicals, including pharmaceuticals, dyes, herbicides and pesticides. Industrial process of anilines production by reduction of nitrobenzenes using Fe/HCl as a reductant (Bechamp reaction) is no longer viable due to the generation of significant amounts of toxic wastes. The liquid-phase hydrogenation of nitrobenezenes would be a “green” alternative to this process [1]. Under batch conditions, supported gold catalysts (Au/TiO_2, Au/Al_2O_3, Au/Fe_2O_3) provide the highly selective hydrogenation of nitrobenzenes to the corresponding anilines [2-3]. Meanwhile, continuous flow processes are more efficient than standard batch protocols and offer much higher throughput, better control of process variables and less waste levels [4]. Herein, we present the results of the study on the selective nitro group hydrogenation in nitroarenes containing halogens, C=C or C=O bonds over the nanosized Au/Al_2O_3 catalyst under continuous-flow conditions.

A series of the 2.0% Au/Al_2O_3 catalysts with different mean diameters of Au particles ranging from 1.8 to 6.6 nm was prepared by changing some parameters in the standard ”deposition-precipitation” procedure [5]. The catalytic activity was tested using the H-Cube Pro instrument equipped with a continuous-flow reactor at 60-110 °C and 10-20 bars of H_2. A 0.05 M solution of nitro aromatic compound (3-nitrostyrene, 4-nitroacetophenone, 2-, 3- or 4-chloronitrobenzenes) in toluene containing *n*-decane (0.5 vol. %) as the internal standard was fed into the reactor at the flow rate of 0.5 $mLmin^{-1}$ and mixed with H_2 supplied through the catalyst bed at the rates of 8.4-60 $mLmin^{-1}$. The reaction products were analyzed by GC and GC-MS. As an initial step, the process conditions at which the apparent reaction rate does not affect by external diffusion have been determined. Under these conditions, hydrogenation of chloronitrobenzenes over the Au/Al_2O_3 catalysts gives the corresponding chloroanilines with almost 100% yield, formation of any dechlorination products being not detected at all. Increasing the reaction temperature suppresses the intermediate formation of nitroso compounds and condensation products which may poison the catalyst. Hydrogenation of 3-nitrostyrene and 4-nitroacetophenone carried out in a flow reactor leads to the formation of 3-vinylaniline and 4-aminoacetophenone with 90% and 97 % yields, respectively, at very mild conditions. Among the catalysts with different gold dispersion, the highest TOF for hydrogenation of 3-nitrostyrene was characteristic of the samples bearing Au particles of 2–3 nm in size. In addition, the effect of steric peculiarities in the functionalized nitrobenzenes on the rate of their hydrogenation over the Au/Al_2O_3 catalysts was examined. Rising the reaction temperature favors hydrogenation of C=C and C=O bonds to the detriment of selectivity on the target anilines. Under all conditions, the catalyst activity continuously decreases during a catalytic run, probably, due to the agglomeration of Au nanoparticles proceeding by “Ostwald ripening” mechanism.

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The effect of annealing on the structure and morphology of the porous anodic oxide films on Ti-Al powder alloy

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In the present paper we summarize our data on (i) fabrication of self-organized porous oxide films via anodizing of Ti-Al powder alloy; (ii) thermally activated structural transformations of these films.

The investigation of anodic oxide films(AOF) on Ti-40wt%Al powder alloy obtained via anodization in 1M H_2SO_4 containing 0.15 wt% HF and water-free electrolytes on the base of ethylene glycol added NH_4F was carried out. In order to investigate the effect of heat treatment on the atomic and mesoscopic structures the as-grown AOF were annealed in either air or in air-free (10-2 Pa) at T=280-820 °C.

X-ray diffraction, electron microscopy (TEM &SEM) and atomic force microscopy (AFM) were used to analyze the structure of these films on two scales: atomic (mutual atom arrangement) and mesoscopic (mutual pore/tube arrangement).

It has been demonstrated that the anodization of Ti-40wt%Al powder alloy in fluoride containing electrolytes under special conditions leads to the formation of the stable nanoporous oxide on the alloy surface. The as-anodized oxide films are X-ray amorphous.

The correlation of morphological changes with the crystallization state of annealed oxide films was discussed. It has been shown that the crystallization is achieved through thermal treatment at 700-820 °C. In air and air-free annealing up to 820 °C regular nanoporous mesoscopis structure still remains. The crystal structure of air annealed AOF corresponds to the mixture of anatase (for the most part) and rutile as well as Al_2O_3 whereas air-free annealing result in primarily anatase phase TiO_2 and Al_2O_3 and reduced titanium oxides Ti_2O_3, TiO. Finally the possible applications of the developed materials as photocatalysts are considered.

Kinetic features of olefins polymerization over titanium-magnesium catalysts

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The catalyst is a vital part in technology of the polyolefins production. About 90% of polypropylene and 40% of polyethylene in industry are produced with the usage of titanium-magnesium catalysts (TMC). These catalytic systems are composed of titanium chloride ($TiCl_4$) supported over magnesium chloride ($MgCl_2$). TMC used for stereospecific polymerization of propylene besides support and active component including stereoregularing electro-donor additives: internal donor (ID), being added to the content of supported catalyst and external donor (ED), being added to the reaction medium with aluminum organic activator. Electro-donor compounds ID and ED play the key role in assurance high level of stereospecific of TMC.

In spite of general application of TMC, data of kinetics polymerization ethylene and propylene over these catalysts are not full enough. Particularly the well known feature of TMC is that these catalysts containing a set of active centers, having various kinetic characteristics and producing of polymer chains with varied molecular mass. Along this in literature the information about distribution of active centers, producing polymer with various molecular mass and stereoregularity, of reactivity in reaction of propagation chain is almost absent. The reception of these data require application of special techniques and has a great interest in analysis of mechanism olefin polymerization over TMC.

In present work the number of active centers (C_P) and propagation rate constants (k_P) for separate groups of active centers in ethylene and propylene polymerization over TMC were determined. In the work the method of inhibition polymerization with radioactive carbon monoxide was used followed by division of polymers on fractions which differ in molecular mass and stereoregularity, and analysis of these fractions using the method of gel-chromatography.

It was found that examined TMC produce polymers with broad molecular weight distribution (MWD) (M_w/M_n = 4.0-5.1) which shows their multisite nature. Polyethylene obtained (PE) was separated in single fractions which have narrow MWD (M_w/M_n = 1.3–1.6) and differ in molecular mass by more than an order. With growth of molecular mass of fraction polymer it is observed the reduction of number of active centers, producing these fraction, and increasing of propagation rate constant of these centers. Thereby active centers producing high molecular weight fraction of PE have the maximum reactivity (value k_P). At the same time the content of such active centers in catalyst is much less than the content of centers that produces low molecular PE with less reactive ability. In case of propylene polymerization the data about number of active centers and propagation rate constants for centers that produce fractions of polymers with different stereoregularity was received. Distribution of active centers different by stereospecificity of reacting ability in the reaction of growth of polymer chain was found.

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The catalytic properties of mixed $Ag_2Cu_2O_3$ oxide

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The compounds with paramelaconite phase structure like $Ag_2Cu_2O_3$ and Cu_4O_3 attract a great attention in the last few years. It caused by its unique electronic and magnetic properties [1,2]. The crystal lattice of $Cu_4O_3/Ag_2Cu_2O_3$ compounds contains two unequivalent oxygen species signed as Cu^{2+}-O-Cu^{2+} and Ag^{+}(Cu^{+})-O-Cu^{2+} with different electronic properties explaining the perspectives of paramelaconite materials in catalytic applications. For example, a few papers devoted to the catalytic activity of Cu_4O_3 and $Ag_2Cu_2O_3$ have already been published [3,4]. However, there is not enough data concerning the evolution of paramelaconite structure. Also, the role of different oxygen species under catalytic conditions can not be found in literature. Pure $Ag_2Cu_2O_3$ can be prepared by simple coprecipitation method, while the synthesis of Cu_4O_3 phase is difficult [5]. This work is devoted to the study of $Ag_2Cu_2O_3$ with paramelaconite structure during catalytic CO oxidation. The complex of physicochemical methods such as TEM, XPS, XRD, TPR and TPD-He was used to characterize the structure and properties of mixed silver-copper oxide. Also, DFT theory was applied to calculate the energy of oxygen vacancy formation.

The sample of $Ag_2Cu_2O_3$ was synthesized by the coprecipitation of Ag^{+} and Cu^{2+} nitrate salts in alkali conditions. Using TEM method it was shown that $Ag_2Cu_2O_3$ sample consisted of sheet-like particles with ~80 nm of width and ~200 nm of length. During TPD-He study the start of thermal decomposition of $Ag_2Cu_2O_3$ oxide was observed at approximately 280°C. Based on XRD data the mixed silver-copper oxide decomposed into Ag and copper oxide phases that was also confirmed by the calculation of evoluted molecular oxygen during TPD-He quantity.

Catalytic properties were investigated in flow reactor with contact time of reaction mixture equal to 0.015 sec (GHSV=240000 h^{-1}). Prepared $Ag_2Cu_2O_3$ possessed the high catalytic activity with the start of CO oxidation at ~40°C, while 100% CO conversion was observed at 140°C. The excellent stability of $Ag_2Cu_2O_3$ catalytic properties was demonstrated during a few heating-cooling cycles from room temperature up to 200°C. XRD study of $Ag_2Cu_2O_3$ after catalytic CO oxidation showed the preservation of paramelaconite structure, while the surface of $Ag_2Cu_2O_3$ was partially reduced as XPS showed.

Mixed $Ag_2Cu_2O_3$ oxide was also studied by XPS during the heating in oxygen up to 200°C. At the first stages of the heating in O_2 the surface reduction of $Ag_2Cu_2O_3$ was observed due to the presence of carbon-containing surface admixtures. Prolonged heating at 225°C in O_2 resulted in the significant decrease of surface carbon after what the reoxidation of $Ag_2Cu_2O_3$ was started. The surface reduction by carbon-containing species was deeper than in case of catalytic conditions. The reduction of $Ag_2Cu_2O_3$ with metallic silver particle formation was also occurred under the exposure of electron beam during TEM analysis immediately in the microscope chamber.

The reduction of $Ag_2Cu_2O_3$ during TPR-CO study was found to be complex. Corresponding TPR-CO curve was characterized by the appearance of low-intensive shoulder from 40 to 115°C and high-intensive peak from 120 to 300°C. The temperature region of low-intensive shoulder coincided with those of catalytic CO oxidation indicating the great importance of weakly bound oxygen species for low-temperature catalysis. The high catalytic activity of $Ag_2Cu_2O_3$ near room temperature can be related to highly reactive oxygen species at the surface. There are two unequivalent oxygen species within $Ag_2Cu_2O_3$ structure: oxygen surrounded by four Cu^{2+} ions (signed as Cu^{2+}-O-Cu^{2+}) and oxygen bounded with two Ag^{+} and two Cu^{2+} ions (signed as Ag^{+}-O-Cu^{2+}). It seems that former oxygen can be reversibly reduced with formation of Cu^{1+}-[ ]-Cu^{2+} vacancy due to effortless Cu^{1+}/Cu^{2+} Ox-Red transition, while the removal of latter oxygen species can likely result in the destruction of paramelaconite structure followed by the formation of metallic silver particles. To examine this hypothesis the energies of oxygen vacancy formation were calculated using DFT theory for discussed oxygen species at the (001) crystal face of

$Ag_2Cu_2O_3$ structure. For removal of oxygen from Cu^{2+}-O-Cu^{2+} position approximately 2.53 eV is required, while the energy of Ag^{+}-[ ]-Cu^{2+} formation is significantly higher and equal to 3.30 eV. So, surface oxygen from Cu^{2+}-O-Cu^{2+} position may be responsible for low-temperature CO oxidation over $Ag_2Cu_2O_3$. The interaction of this oxygen species with CO results in the reversible reduction of divalent copper into monovalent state with the preservation of paramelaconite structure while the strong reducing conditions can result in destruction of paramelaconite structure by means of the removal of Ag^{+}-O-Cu^{2+} oxygen followed by the appearance of metallic silver particles. However, to establish the role of different oxygen species at the surface of $Ag_2Cu_2O_3$ in low-temperature catalysis the additional ***in situ*** experiments should be carried out.

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The study of acidity of boric acid modified γ-aluminas by probe EPR-spectroscopy

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The surface acid sites of oxide catalyst supports such as electron acceptor (Lewis) or proton donor (Brönsted) sites play essential role in the adsorption and catalytic properties of the materials. Thermally activated γ-Al_2O_3 has found broad application as catalyst support (or as catalyst in some processes) due to ability to vary its properties, such as Lewis/Brönsted acidity, by the introduction of different modificators. It has been recently founded [1] that NiO/γ-$Al_2O_3 \cdot B_2O_3$ catalysts demonstrate high activity in ethylene oligomerization reaction. So it’s important to determine the influence of B_2O_3 content on the acidity of modified supports.

The acidity of oxide supports may be characterized by a great variety of physicochemical methods (for example, IR of the hydroxyl groups and probe molecule adsorption, TPD of ammonia e.t.c.). In addition, electron paramagnetic resonance (EPR) spectroscopy spin probe technique may extend the qualitative and quantitative information about acid surface sites and describe dynamics of adsorbed species [2,3]. Nitroxyl radicals, for example 2,2,6,6-Tetramethyl-piperidin-1-yl-oxyl (TEMPO), or aromatic molecules with low ionization potential, such as anthracene and its derivatives, are widely used for this purpose [4,5].

The samples of γ-$Al_2O_3 \cdot B_2O_3$ with 10, 15, 20, 30 % wt of B_2O_3 and pristine alumina were prepared from pseudoboehmite suspension by the mixing with solid H_3BO_3 followed by drying and calcination at 600^oC for 16 hours. EPR measurements were carried out on Bruker EMXplus X-band (~9.7 GHz) spectrometer with ER 4105DR resonator. Quartz ampoules with ~30 mg of each sample were activated at 600^oC for 4 hours on air and after fast cooling to ambient temperature were treated with probe solution ($5 \cdot 10^{-4}$ M TEMPO in *n*-hexane or $5 \cdot 10^{-2}$ M 9,10-antraquinone or antracene in toluene). The concentration of paramagnetic species formed from anthraquinone and anthracene on supports surfaces after their heating at 70-80^oC was determined by double integration of the EPR spectra using a single crystal of $CuSO_4 \cdot 5H_2O$ as a standard. A solution of pyridine in hexane ($5.1 \cdot 10^{-2}$ M) was used for titration of TEMPO complex with coordinatively unsaturated aluminum.

The decomposition of TEMPO molecule on a boric acid modified γ-aluminas indicates the increasing of proton donor sites number with the increasing of boric oxide content, furthermore, the relative concentration of accessible Lewis acid centers decrease (from EPR spectra). These effects make unavailable the direct measurement of coordinatively unsaturated aluminum concentration using TEMPO/pyridine in contrast to pristine alumina. The same results were obtained when anthraquinone was used as a probe. The concentration of formed paramagnetic complexes were underestimated and it hardly fitted with real concentration of electron acceptor sites. The application of anthracene molecule may raise these limitations due to its higher sensibility to proton donor sites and stability of formed radical cation in acidic media.

All measurements were carried out on the instrumental base of Omsk Research Collaboration Centre SB RAS.

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Sol-gel synthesis of catalytically active mesoporous aluminosalicates without using templates

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Large potential for a variety of chemical conversions of organic compounds provide catalytic systems based on zeolite – the microporous crystalline aluminosilicates. However, it appears that the zeolites due to the small pore size of [1] unsuitable for catalytic reactions of molecules larger than 10Å.

Expected for the larger molecules will be effective mesoporous mesophase aluminosilicates (MMM) [2], which synthesis is based on the coprecipitation of aluminum and silicon precursors with a surfactant, which is accompanied by self-assembly of liquid crystal mesophases. However, it turned out that due to the synthesis of highly acidic ($pH < 2$) or highly basic medium ($pH > 10$) in the silicate network. aluminum is hardly incorporated. Aluminosilicates obtained by this method have low acidity, are easily broken under the influence of components of the reaction mixture, and their use for the synthesis of the templates are quite expensive.

This work deals with the synthesis of mesoporous aluminosilicate with ratio $SiO_2/Al_2O_3 = 20, 40, 80$ having a narrow pore size distribution and a high proportion of aluminum embedded in a silica lattice without using templates.

Aluminosilicates have been prepared by sol-gel synthesis using tetraethyl orthosilicate and a hydroalcoholic solution of aluminum nitrate [3].

Characterized using X-ray diffraction, MAS NMR ^{27}Al, ^{29}Si, low-temperature nitrogen adsorption-desorption and temperature-programmed desorption of ammonia. Catalytic properties of the obtained mesoporous aluminosilicates tested in the oligomerization reaction of 1-octene. The reaction is carried out continuously in rotating autoclaves at 150-200 °C. The content by weight of catalyst based on the olefin content of 10-30%.

The synthesized amorphous aluminosilicate having a specific surface area of from 500 to 700 m^2/ g, a mesopore volume of 0.85 to 1.0 cm^3/ g, pore size of from 2 to 5 nm, and the acidity of the ammonia from 300 to 750 mlmol/g, which is due to a high proportion incorporated of aluminum.

The influence of the physicochemical characteristics of the obtained aluminum silicates and oligomerization conditions for the conversion of 1-octene and the selectivity of the formation of oligomers is studied.

Determining the product of oligomerization of 1-octene in the presence of mesoporous aluminosilicate catalysts are oligomers with a degree of oligomerization $n = 2\text{-}4$. Conversion octene studied conditions ($T = 150\text{-}200$ °C, $\tau = 3\text{-}5h$) reaches 100%, the selectivity of dimers - 40 ÷ 55%, trimers - 25 ÷ 35%, tetramers - 5 ÷ 15%.

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Синтез пористых материалов взаимодействием наночастиц Al/Fe с водой

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Железосодержащие частицы используются в различных каталитических процессах, таких как селективное окисление сероводорода, дегидрирование этилбензола в стирол, конверсия природного газа и др. Оксид алюминия представляет большой интерес как носитель для катализаторов. Важной характеристикой катализаторов также является наличие активной фазы в наноразмерном состоянии, распределенной равномерно по поверхности носителя. Основной метод нанесения активной фазы – пропитка носителя солями металлов, например, железа, с последующей термообработкой. Существует потенциальная возможность получать катализатор или носитель с равномерно распределенной активной фазой в одну стадию, используя в качестве прекурсора электровзрывные биметаллические наночастицы Al/Fe. Известно [1], что продукты взаимодействия с водой электровзрывного нанопорошка алюминия обладают объемной структурой в виде цветка, высокой пористостью и удельной поверхностью. В связи с этим актуально изучение взаимодействия с водой биметаллических наночастиц Al/Fe и физико-химических свойств полученных продуктов.

Исходные частицы Al/Fe были получены методом электрического взрыва в атмосфере аргона скрученных между собой алюминиевой и железной проволок при содержании металлов в скрутке Al:Fe 50:50. Частицы имеют сферическую форму, средний размер 80 нм, удельную поверхность 8 м^2/г, включают фазы Al и интерметаллидов AlFe и $AlFe_3$, что согласуется с диаграммой состояния системы Fe – Al [2]. Наночастицы химически активны и взаимодействуют с водой уже при 60 °C, как и электровзрывной нанопорошок металлического алюминия. Реакция является экзотермической, сопровождается выделением водорода и изменением pH реакционной среды.

В результате превращения в течение 60 мин образуются объемные пористые частицы с удельной поверхностью 150 м^2/г. Изотерма адсорбции-десорбции полученных структур относится к IV типу с характерной петлей гистерезиса в области капиллярной конденсации. Размер мезопор составляет 4−10 нм. Продукты реакции представлены фазами псевдобемита, оксида железа и фазами интерметаллидов, которые не реагируют с водой в условиях эксперимента. По данным просвечивающей электронной микроскопии, частицы имеют форму нанолистов толщиной 5-8 нм и размерами 100-200 нм, и клиновидных свитков размером 1,5-3,0 мкм. Аналогичные структуры образуются при длительной экспозиции в маточном растворе продуктов взаимодействии с водой электровзрывного нанопорошка алюминия. По данным сканирующей электронной микроскопии частицы объединены в сферические пористые агломераты, размером 0,5–5,0 мкм, окруженные пластинчатыми структурами размером более 1,5-6,0 мкм. Энергодисперсионным анализом установлено, что алюминий и железо равномерно распределены по всему объему агломератов.

Таким образом, электровзрывные биметаллические частицы Al/Fe вступают в реакцию с водой в мягких условиях с образованием объемных пористых структур с высокой удельной поверхностью.

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Синтез медьсодержащих наноструктур AlOOH

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Нанопорошок Al, полученный методом электрического взрыва проводника в атмосфере аргона, легко взаимодействует с водой с образованием наноструктур AlOOH в виде «цветка». Высокая удельная поверхность (около 250 м^2/г) и мезопористая структура делают его перспективным материалом для носителей и катализаторов. Развитие метода электрического взрыва проводника сделало возможным получение биметаллических частиц, в частности, Al/Cu. При сохранении химической активности алюминия в данных частицах, продукты их реакции с водой будут представлять пористую структуру бемита AlOOH с включениями меди. Данные медьсодержащие наноструктуры могут быть интермедиатом при получении катализаторов.

В данной работе исследовали реакцию с водой двух образцов наночастиц Al/Cu с массовым соотношением Al:Cu 20:80 и 40:60 %. Образцы были получены методом электрического взрыва в атмосфере аргона скрученных между собой алюминиевой и медной проволок различных диаметров. Частицы Al/Cu имеют сферическую форму и размеры 80-120 нм независимо от состава. Согласно данным EDAX-TEM анализа, алюминий и медь равномерно распределены по объему частиц. Методом РФА установлено присутствие в образцах фаз Cu_2Al, Al, Cu, Cu_4Al и Al_9Cu, что соответствует диаграмме состояния системы Cu–Al [1]. Алюминий в составе образцов химически активен и взаимодействует с водой уже при 60 °C с выделением водорода. Присутствие меди приводит к сокращению индукционного периода и ускорению реакции, протекающей по механизму электрохимического окисления алюминия. Сложная форма кинетических кривых выделения водорода с тремя максимумами обусловлена, вероятно, неоднородной структурой композитных наночастиц. Зерна фазы алюминия расположены случайным образом между фазами интерметаллидов и меди и имеют различную доступность для воды.

Продукты реакции представляют собой пористые частицы из нанолепестков 100-300 нм шириной и 5-7 нм толщиной, окружающих структурно неоднородные электронно-плотные сферические включения. Нанолепестки аналогичны продуктам окисления в тех же условиях электровзрывных нанопорошков Al и Al/AlN [2]. Электронно-плотные включения обогащены медью, и состоят из блоков размером менее 10 нм. Пористые частицы содержат плохоокристаллизованный псевдобемит, медь и интерметаллиды в тех же соотношениях, что и в исходных нанопорошках. Площадь удельной поверхности продуктов реакции с водой образца, содержащего 20 % Al, составила 31 м^2/г, образца с 40 % Al – 130 м^2/г. Можно предположить, что в исходных наночастицах Al/Cu фазы меди и интерметаллидов находятся в виде включений размером менее 10 нм и контактируют с расположенными между ними включениями фазы алюминия. При реакции алюминия с водой и образовании пористых продуктов частица композита увеличивается в размере, медьсодержащие включения смещаются, но сохраняют размер, форму и относительно равномерное распределение по объему частицы.

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Dissociative and physical adsorption of reagents for the catalytic hydrogenation of unsaturated aldehydes on Pt nanoparticles. A quantum chemical study

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Heterogeneous supported nanocatalysts represent a prospective class of advanced materials which can possess advantages over the common used in industry catalysts: 1) the selectivity can be tuned by surface modification, 2) enhanced stability in the operational conditions, 3) low price of the catalytic systems of similar performance. One line of developments of the novel catalysts is nanoparticle preparation via sol-gel method with surface modification by bulky or long chain ligands grafting onto the nanoparticle. As was demonstrated in [1], the results for hydrogenation of unsaturated aldehydes to unsaturated alcohols on capped Pt nanoparticles (NP) are encouraged. However, the fundamental mechanisms are still unknown. In the current work, the elementary steps of such a catalytic reaction, i.e., croton aldehyde hydrogenation, were studied within the cluster models of Pt surface using the DFT quantum chemical calculations. The main study was conducted with BLYP density functional in conjunction with the CRENBS shape consistent pseudopotential with spd–basis functions for Pt atoms and 6-31G(d,p) basis set for the remaining atoms. The Pt_{25} clusters consisting of two layers of Pt atoms were used as models of the Pt NP surface (Pt(100) facet). The diameter of the Pt_{25} cluster is close to 12 Å which agrees well with the size estimates for experimentally prepared Pt NP [1]. The justification of the computational level was based on comparison of the computational results for Pt_4 cluster on different theory levels, i.e., the PBE, PW91, and HSE density functionals in conjunction with CRENBS, cc-pVDZ-PP, LANL2DZ, and Stuttgart RSC 1997 pseudopotentials.

The different spin states of the clusters were considered (spin multiplicity up to 11). The adsorption of reagents (H_2 and aldehydes) and the organic ligands (BuSH, Bu = n-C_4H_9) working as orienting agents were studied as initial steps of the catalytic process. The various kinds of adsorption were studied: (1) physical adsorption of H_2 on different sites of Pt_n clusters; (2) adsorption of H_2 resulting in the Pt-adsorbed H atoms with η^2 and η^1 chemical bonds; (3) dissociative adsorption of BuSH of forming chemically bounded ligands in the Pt_{25}-$(SBu)_x$ compounds and the neighboring –SBu/H adsorbed pairs; (4) aldehyde adsorption on the neat Pt surface and the bare surface. For all these pre-reaction surface complexes, the molecular structures, adsorption energies, and vibrational frequencies were studied. It was found that the ground state of the Pt_{25} clusters is the quintet one with the typical spread of energies in lower spin states (M=1,3,5, and 7) of about 3 kcal/mol. The dissociative adsorption energy of H_2 was estimated as 5-9 kcal/mol in a reasonable agreement with available experimental value of about 16 kcal mol^{-1} [2]. At the same time, the –SBu group formation energy was estimated as 30-56 kcal mol^{-1} depending on the adsorption mode, i.e., η^2-,η^3-, and η^4-bonds between Pt and S atoms. The estimated surface coverage of about 4/9 monolayer (ML) is in reasonable agreement with the experimentally observed dependence of hydrogenation kinetics on the surface coverage [1]. One can believe that the obtained here value (4/9 ML) is a lower limit estimation since Pt (100) facet is the most closest packed one. The simulated IR-spectra of CO adsorbed onto the Pt NP and experimental DRIFTS spectra are in general coincidence. Thus, the proposed model can be employed for further study of mechanism of the catalytic reaction.

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Modified aluminum hydroxide as a precursor for manganese catalysts

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Manganese oxides supported on silica promoted with alkali metals or are high-temperature catalysts for the dimerization of methane to ethylene or oxidative dehydrogenation of alkanes to olefins [1, 2]. In case of joint air and hydrocarbon system MnO_2/Al_2O_3 used as catalysts for deep oxidation of hydrocarbons [3] and for the most part as catalysts for high-temperature incineration. [4] In this case, the high temperature combustion implies that MnO_2/Al_2O_3 system can operate up to 1000 ° C without reducing catalytic activity in the reaction of the complete oxidation of hydrocarbons. For the preparation of manganese-containing hydrocarbon combustion catalysts used methods for preparing a precursor catalyst by impregnation or mixing of aluminum hydroxide or MnO_2 manganese nitrate followed by drying and calcination. A method for producing a catalyst precursor in a single step, obtain an alignment nanofibrous aluminum oxyhydroxide and manganese ions administration (II) in the structure [5], respectively, in the catalyst and is a promising technology for preparing catalysts [6].

The aim is to establish the possibility of the use of aluminum hydroxide as a precursor for the high-temperature catalysts in the complete oxidation of methane.

In operation precursors were synthesized with different contents of manganese (II) from 0.5 to 10.5 wt. %. The phase composition of the resulting amorphous precursors and very well defined only phase AlOOH, Al_2O_3 and metallic Al. Eigenphases manganese was found.It has been shown that the catalytic activity is extremely low freshly prepared samples or does not appear. Experiments have been conducted on the effect of thermal activation derived precursors in air at 850 ° C. After calcinations, the phase composition changes. XRD analysis results showed that, depending on the concentration of manganese ions (II) to form various structures precursor aluminum. For a sample with a manganese content of 3.2 wt. %. Mixture of oxides formed - rhombohedra Al_2O_3 and Al_2O_3 (alumina). For a sample with a manganese content of 5.7 wt. % Formed nonstoichiometric oxygen σ-Al_2O_3. For a sample with a manganese content of 10.5 wt. % Is formed by α-Al_2O_3.

It was ascertained that the most promising catalyst for methane high-temperature combustion is a system with manganese content in the precursor 5.7 wt. %. This catalyst does not change its phase composition during the operation; 50 % methane conversion is achieved at 530 °C, as compared with the system with manganese content in the precursor of 10.5 wt. % , where 50 % conversion is achieved at 680 °C.

Use of the catalyst with manganese content of 5.7 wt. % allows you to run and to turn heat convectors autothermally when heating catalyst bed to 500–530 °C.

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Design of easy and efficient procedure of the synthesis of surface modified zero-valent iron nanoparticles

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Magnetic materials, including nanoparticles (NPs), actively attract attention of scientists in the past decades due to their unique physical and chemical properties and possibility of widespread application. Modification of magnetic materials enables to solve a number of high priority problems in medicine and pharmacology [1]. The principal biomedical application scopes of magnetic NPs are design of biosensors, magnetic resonance imaging, targeted drug delivery, catalysis and controlled local hyperthermia. Nowadays there is a need to enhance the properties of nanomaterials by grafting with different organic functional groups. Aromatic diazonium salts are proved to be excellent modification agents for modification of different surfaces. Arenediazonium tosylates (ADTs) have several advantages over classic aromatic diazonium salts [2]. ADTs are useful organic agents for the surface modification of the carbon and metal surfaces [3] because of the easiness of synthesis, the possibility of fast electrolytic reduction, a wide range of functional group in the diazonium salt molecule and the possibility to stable covalent binding with the surface.

We reported an original and simple in situ method to synthesize spherical magnetic zero-valent iron NPs by room temperature reduction of iron chloride salts in the water and in the presence of arenediazonium tosylates. Organic functional groups were covalently grafted on surface of zero valent iron. This process is unique and has a high scientific value, as for today in order to obtain zero valent iron NPs, high temperature and pressure, two-phase systems or even surface-active compounds are usually employed.

Iron NPs have been characterized by FT-IR spectroscopy, XRD, TEM, DTA/TGA/DSC and BET low-temperature nitrogen absorption method. Obtained NPs with average particle size of approximately 10 nm possess a high oxidation resistance, aryl layers protect NPs structure up to 250 °C. Developed strategy allows to realize efficient and easy synthesis of metallic iron functionalized NPs. We conclude that this approach can be applicable for the medicinal researches due to the low price of the precursors, water as solvent for reaction, the anticipated high magnetic moment, the stable covalent binding and the possibility to change functional groups in ADT molecule. We also believe that this novel synthetic approach will not only pave a new way for the preparation of iron NPs but also provide a general functionalization strategy for zero-valent metal NPs

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Activity of original Hoveyda-Grubbs II catalyst in ring-opening metathesis polymerization of exo,exo-2,3-dicarbomethoxy-5-norbornene in two different solvents

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Ring-opening metathesis polymerization (ROMP) is a convenient method for synthesis a range of polymers from cyclic olefins. This process allows preparing good performed polymers. Recently the interest of researchers was focused on 2,3-dicarboxy-5-norbornene acid derivatives as a possible raw material for ROMP polymers preparation[1-3]. Now this polymer is used in glues production, as well as in manufacturing of decorative, insolation and electrical products [4-6]. Reaction injection molding (RIM) is a method for producing material by ROMP. Polymerization rate is a significant parameter of RIM process, and generally it should be high. ROMP process rate, mainly, depends on an olefin and a catalyst structures. Additionally their structures affect the mechanism and pathway of the reaction. Therefore the kinetic parameters are important for the deep understanding of the process and definition of the optimal operation parameters for industrial facilities.

In this work, we have studied activity of original Hoveyda-Grubbs II catalyst which contain N-chelating ligand in exo,exo-2,3-dicarbomethoxy-5-norbornene polymerization in two different solvents [7]. We found that the catalyst has twice higher activity in chloroform-d than in toluene-d8. Dielectric constants of these solvents differ more than twice. Previously Grubbs et al. disclosed that the initiation rate constant for ruthenium catalysts is roughly proportional to the dielectric constant of the reaction solvent [8]. This effect can be explained by stabilization of the 4-coordinated state active species of ruthenium in more polar solvents after phosphine dissociation step. In fact the dissociation is a more appropriate mechanism of catalyst activation for Grubbs I group than others. Hoveyda-Grubbs II catalysts have rather interchange than dissociative mechanism [9]. Both dissociative and interchange mechanisms have different activation parameters. For Hoveyda-Grubbs II dissociative mechanism by a high enthalpy and positive entropy and vice versa interchange mechanism is characterized by low enthalpy and negative entropy [10]. Values of these variables in the two solvents were measured. We found that the entropy has a negative magnitude in both solvents chloroform-d ($\Delta S^{\neq} = -109{,}2$ J/mol×K) and toluene-d8 ($\Delta S^{\neq} = -50{,}4$ J/mol×K) and enthalpy in chloroform-d ($\Delta H^{\neq} = 62{,}3$ kJ/mol) is less than in toluene-d8 ($\Delta H^{\neq} = 82{,}9$ kJ/mol). Due to the fact that the entropy is decreased we can conclude that formation of the transition state does not include the step of dissociation. Due to solvatation effect both parameters enthalpy and entropy are lower in toluene-d8 then in chloroform-d thereby providing lower reactivity in toluene-d8. We can also suppose that the intermediate is polarand for that reason it is better stabilized in chloroform.

We have established that the activity of the catalyst is twice more in chloroform-d than in toluene-d8thatcan be explained by the effect of solvatation.

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Influence of ZrO_2 and Al_2O_3 addition on activity of Cr/SiO_2 catalysts of isobutane dehydrogenation

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Many industrial catalysts are composed of one and more active components supported on the surface of different supports. State and dispersion of active components influence on catalytic properties and depend on many factors. The introduction of the active component on the support surface is the determinative step of the catalyst preparation. Distribution of active component on the surface of support and its state may be controlled by changing of properties of support surface, porosity, the precursor nature and amount of the component introduced.

Silica is one of the most common supports for heterogeneous catalysts because of wide range of specific surface area and pore volume. The pore size of silica can be changed in wide range on the preparation step or due to following hydrothermal treatment. However, the application of silica supports is limited by inability of active component stabilization in desirable state. Therefore, the modifying of silica by oxides, having suitable surface properties, is one of the ways to improve the properties of catalysts on the basis of this support. The alumina and zirconia are ones of appropriate modifiers for many catalysts.

The aim of this work is to study the distribution of modifying oxides (alumina and zirconia) on the surface of silica, depending on the amount of introduced oxide, and silica pre-treatment conditions, as well as activity Cr-containing catalysts on the basis of these supports in the dehydrogenation of isobutane. The silica with wide mesopores (10-50 nm) was used as the primary support, providing the desired porous structure of catalyst. While aluminum and zirconium oxides are used as a secondary carrier, providing the required functional properties of the applied surface active component.

The commercial silica (KSKG) was used as initial support. The series of Al_2O_3/SiO_2 and ZrO_2/SiO_2 supports were synthesized by incipient wetness impregnation using aqueous solutions of $Al(NO_3)_3{\bullet}9H_2O$, and $ZrO_2(NO_3)_2{\bullet}2H_2O$. SiO_2, Al_2O_3 and ZrO_2 supports were taken for preparation of pattern Cr-containing catalysts. Cr-containing catalysts with loading of Cr_2O_3 corresponding one monolayer were prepared by impregnation of support with water solution of CrO_3.

It was shown that introduction of Al_2O_3 led to formation of porous structure with bimodal pore size distribution. Formation of alumina with pores of 2-8 nm took place inside wide pores of initial silica. Introduction of zirconia lead to insignificant changing of porous structure of silica. It may be associated with formation of layer of zirconia on the surface of silica support.

The catalytic activity in reaction of isobutane dehydrogenation decreased in row of pattern catalysts $Cr/ZrO_2 > Cr/Al_2O_3 > Cr/SiO_2$. It was shown that activity increased with increasing of Al_2O_3 loading in $Cr/Al_2O_3/SiO_2$ catalyst. And activity of catalysts on the basis of 40% wt. Al_2O_3/SiO_2 was higher that one for Cr/Al_2O_3 catalysts. That may be associated with bimodal porous structure of Al_2O_3/SiO_2 support. Also, it was shown by UV-vis spectroscopy and TPR that addition of Al_2O_3 and ZrO_2 provided stabilization of Cr (VI). Reduction of Cr (VI) species leads to formation of Cr_2O_3 clusters high active in reaction of dehydrogenation.

Thus, the addition of ZrO_2 and Al_2O_3 leads to increasing of activity of Cr/SiO_2 catalysts in reaction of isobutane dehydrogenation.

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On the form of the kinetic curve and dimensioning hydrogenation reactions on highly porous catalysts

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Experimental basis for the calculation of the kinetic parameters of the liquid phase hydrogenation reactions are time dependence of the absorbed hydrogen amount. However, the data dependence quantitatively reflect the totality of the catalytic reaction with hydrogen and can be used to analyze patterns of reactions studied only as effective values. In the case of multistep process effective values include both the rate of chemical reactions and secondary processes accompanying hydrogenation: reduction of the oxidized surface sites of the catalyst or dehydrogenation of solvents, etc.

It can be argued that the curve of hydrogen absorption during the reaction is characteristic of the gross, while the concentration dependences relate to individual characteristics, i.e. to one or another component, quantitative relationships between them will be determined by the stoichiometry of the reaction. In general, the observed rate of the reaction, calculated from the amount of absorbed hydrogen can be equal to the speed calculated by the change in concentration of the starting compound or reaction product. Concentrations of substances and their changes over time are the only source of information about the reaction system and its temporal evolution. The main task of kinetics is experimental determination of the reactant and product concentrations or more precisely their changes to determine the rate of the chemical reaction itself. From this perspective, it is extremely important to study approaches to the use of the experimental curves for the correct calculation of the kinetic adsorption and diffusion parameters of the studied reactions. Calculation of these parameters from experimental data is only possible when there are more broad spectrum of dependency, in particular, the observed reaction rates of the catalyst and its amount of dispersion, the concentration of the starting reagent, the hydrogen pressure.

Kinetic study is of paramount importance, not least because the kinetic curve is a consequence of the reaction mechanism. According to the author’s point of view [1], in the case of hydrogenation processes form the kinetic curve can answer the five most characteristic types. It is possible that for the same reaction, depending on the conditions of, for example, changing the initial amount of compound to be hydrogenated, the kinetic curve shape may vary, e.g., due to change in the limiting step, side reactions, the main reaction of the transition from one region macrokinetic another. However, the main purpose of the kinetic curve, and there is calculation of the kinetic parameters of the process.

For the kinetic parameters determination individual plots on the kinetic curve are divided into three parts. For every part the reaction rate dependence on the concentration can be described by simple analytical equations. The first part is the region of high concentration where the order for the hydrogenated substance is close to zero. The second part is the region of the low concentration – order of reaction is 1. The last part is the region of the hydrogen and organic compound high-pressure – reaction order is equal to zero. Adsorption, kinetic and diffusion parameters were calculated on the example of the sodium p-nitrophenolate hydrogenation on skeletal nickel in various conditions. The developed approach is extremely important for choosing the process conditions as close to real one.

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On the competitive nature of the adsorption of the initial compound versus the reaction product under hydrogenation conditions

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The kinetics of the nitrobenzene hydrogenation on Raney nickel in aqueous 2-propanol showed that at low concentrations of the initial compound the aniline concentration kinetic curve goes through a maximum. Similar time dependence is observed in case of hydrogenation of other intermediate nitrobenzene reduction products: phenylhydroxylamine, azoxybenzene and azobenzene. It is to be noted that the concentration decay of aniline in the bulk liquid phase at high degrees of conversion of the initial compound is dependent on the solvent composition. It was found that if an aqueous solution of 2-propanol azeotropic composition ($x_2 = 0.68$) under hydrogenation of phenylhydroxylamine, azoxy and azobenzene at the initial compound conversion above 0.9 the drop of aniline concentration was 12, 8 and 7 %, respectively.

On the other hand, addition of acetic acid (0.01 M) leads to decrease of the extremum at the kinetic curve by ca. 30 % in case of phenylhydroxylamine hydrogenation and to its disappearance in case of azoxy- and azobenzene. Carrying out the hydrogenation of mentioned compounds in aqueous 2-propanol with addition of sodium hydroxide ($x_2 = 0.68$, 0.02 M NaOH) leads to the extinction of maximum kinetic curve for all of intermediates. The hydrogenation of nitrobenzene leads to a maximum appearance only in the reaction in an aqueous 2-propanol with addition of an acid ($x_2 = 0.68$, 0.01 M CH_3COOH).

Smoothing or complete disappearance of the kinetic curve maximum for different initial compounds and solvent compositions may be because of several reasons. Solvent pH lowering and oxidation of the Raney nickel active surface leads to fall in the aniline adsorption capacity. The oxidation of the catalyst surface is most characteristic for the hydrogenation of oxygen-containing groups, primarily nitro-. The sodium hydroxide presence in a solvent also promotes the oxidation processes. Thus the hydrogenation of azobenzene having the lowest oxidation potential, with the addition of sodium hydroxide in solvent, results that absorbed hydrogen total amount is 10 % less than required by stoichiometry.

In the absence of competitive adsorbtion between the hydrogen and the organic compound in the low catalytic reaction speed adsorption will occur in conditions close to equilibrium. Based on the material balance and the adsorption equilibrium constants of the initial compound and aniline an equation describing the time dependence of reaction product concentration was found. According to the proposed equation the ratio of the hydrogenation rates near the maximum is mostly determined the adsorption capacities of the system components. Presence of a maximum on the kinetic curves is due solely to the competitive adsorption of aniline and hydrogenated compounds. Calculations showed that for phenylhydroxylamine and azobenzene adsorption coefficients in 210÷1200 times higher than one for aniline. That is the reason why the aniline adsorption becomes possible only at a significantly reduced hydrogenated compound concentration by carrying out of catalytic reaction. Proposed kinetic schemes of the above mentioned compounds hydrogenation taking into account the competitive nature of the adsorption of the initial compounds and aniline satisfactorily describe the experimental results.

Study of kinetics of hydrogen production by catalytic pyrolysis of methane on nickel catalyst

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Production of hydrogen is primarily achieved via catalytic steam reforming, partial oxidation, and auto-thermal reforming of natural gas. These processes are somewhat complex and CO is formed as a by-product, therefore requiring a separation process if a pure or hydrogen-rich stream is needed. As an alternative method, supported metal catalysts can be used to catalytically decompose hydrocarbons to produce hydrogen. The process is known as catalytic pyrolysis of hydrocarbons. Methane, the hydrocarbon containing the highest percentage of hydrogen, can be used in such a process to produce a hydrogen-rich stream. The decomposition of methane (CH_4) occurs on the surface of the active metal to produce hydrogen and filamentous carbon [1, 2]. As a result, only hydrogen is produced as a gaseous product, which eliminates the need of further separation processes to separate CO_2 and CO. Nickel is commonly used in research as a catalyst for methane pyrolysis in the 500-700 °C temperature range. As a sequence of the process, carbon is deposited on the catalyst in the form of carbon filaments but part of the carbon is deposited as encapsulating carbon which causes catalyst deactivation.

In this paper shows the results of experiments, the catalytic decomposition of pure methane at 90% Ni/Al_2O_3 and 82% Ni-8% Cu/Al_2O_3 catalysts. The process temperature was varied in the range of 550-675 ºC and the pressure was 1-10 atm. Catalysts were prepared by two different methods: coprecipitation method and wet combustion. In this paper, the catalysts were investigated by various physicochemical methods. Also, samples of the resulting nanofibrous carbon. Preliminary data showed that a change in pressure, temperature, catalyst composition, a method of preparation of the catalyst varies nanofibrous carbon texture. The paper shows the rate of formation of hydrogen and carbon nanofibrous depending on the pressure and temperature on the Ni-containing catalysts.

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Kinetics of nitrochlorobenzene hydrogenation on palladium and nickel catalysts

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Dehalogenation is a main undesirable process, resulting in the considerable decline of the aminochlorobenzene yield in liquid phase hydrogenation of the corresponding nitro compounds. Kinetic regularities of nitrochlorobenzene hydrogenation in a great deal are determined nature of the catalyst and composition of the solvent. During the leadthrough of process in 2-propanol on palladium catalysts complete elimination of chlorine takes place, while application of skeletal nickel allows to sharply decrease the degree of dehalogenation. Research results showed that most substantially a temperature and composition of the solvent influence on the rate of hydrogenation 2-chloro-4-nitroaniline and on the degree of dehalogenation. It is set that increase of water concentration in composition of 2-propanol-water solvent leads to increasing of the degree of dehalogenation with an insignificant falling of reaction rate. By decreasing the temperature from 338 K to 273 K in hydrogenation process in 2-propanol on skeletal nickel the degree of dehalogenation decreases almost by an order.

Previously it has been shown [1] that the hydrogenation of nitrochlorobenzene isomers flows through a consecutive scheme, and the corresponding amine is formed with a high rate only after a complete conversion of starting nitro compound. Elimination of chlorine occurs most intensively from the amino compound. The resulting chlorine can be adsorbed on the catalyst, so some part of active centers of the surface becomes unavailable for organic molecules. Eventually, during the process decreases both the reaction rate, and the degree of conversion of the source nitrochlorobenzene.

The decline of dehalogenation intensity in the conditions of nitrochlorobenzene isomers hydrogenation, and 2-chloro-4-nitroaniline in particular, can be attained by the change of acid-basic properties of solvent. Introduction to 2-propanol–water solution of small amounts of acetic acid allows to arrive at the lower degrees of elimination of chlorine than in a neutral solvent. Opposite, increase pH of the liquid phase, for example, by introduction of sodium hydroxide, promotes in growth of elimination of chlorine.

Influence of solvent composition shows up through the change of quantitative correlation of individual forms of hydrogen, linked with the active centers of catalyst surface. It is known [2], that the introduction of sodium hydroxide to a composition of liquid phase increases an amount of hydrogen form with high values of the heat of adsorptions (strongly adsorbed forms), while the acid additions in the solvent are instrumental in their decline. Experimental fact of increase of dehalogenation degree at 2-chloro-4-nitroaniline hydrogenation allows making a conclusion that the strongly adsorbed forms of the hydrogen are most active in the elimination of chlorine.

On the other side, introduction to water solution of 2-propanol of the acetic acid decline the degree of dehalogenation, which is to a great extent determined the amount of the entered acid. Most perceptibly the effect of influence of additions of acid on the degree of dehalogenation appears during the leadthrough of process at the lowered temperatures.

The variants of kinetic model of 2-chloro-4-nitroaniline hydrogenation, taking into account possibility of blocking of active centers of catalyst surface by the eliminated chlorine, are offered. Got results showed satisfactory accordance of calculation and experimental data for the different conditions of the process.

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Characterization of electron-acceptor sites on the surface of sulfated alumina using EPR

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Alumina is widely used in catalysis. The surface of the low-temperature Al_2O_3 phases is known to have both acid and base sites of different types. Electron-donor and electron-acceptor sites can be investigated using suitable spin probes. This method is based on using specific molecules which selectively interact with the surface sites yielding surface paramagnetic species.

In the present work, relations between the concentrations of electron-acceptor sites with different strength and concentrations of deposited sulfates were studied. Recommendations on the use of spin probes for testing electron-acceptor sites with different strength were suggested. The mechanism of the polycondensation of aromatic probes on the surface electron-acceptor sites explaining experimental results was proposed.

Sulfated Al_2O_3 samples with the different concentrations of SO_3 (2, 4, 8, 12, 16 wt.%) were studied. Solutions of antracene (4×10^{-2} M), perylene and hexamethylbenzene (2×10^{-2} M) in toluene and pure toluene were used as spin probes.

Two experimental techniques were used. In the first method changes of the concentration of paramagnetic particles over time were monitored at room temperature. The first measurement was carried out immediately after the activation of the sample; the following measurements were carried out every 24 hours during the week. The second technique included a study of the changes in the concentration of paramagnetic particles after heating the activated samples with the probes for 18 hours at 80°C.

It was found that the concentration and the strength of electron-acceptor sites significantly grew with an increase of the sulfate concentration. The strongest electron-acceptor sites tested with toluene immediately after absorption were only detected with a SO_3 concentration 4% or higher. The weakest sites tested with perylene were present on the surface of all the samples, with their concentration on 12% SO_3 sample being 3×10^{19} g^{-1}.

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Исследование механизма процесса окисления алкиларенов кислородом в присутствии комплексов поливалентных металлов, иммобилизованных на полимерную матрицу

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Создание кинетического описания жидкофазного окисления толуола в присутствии нанокатализаторов на основе металлов переменной валентности, инкорпорированных в полимерную матрицу, позволит прогнозировать поведение таких катализаторов и предложить кинетическое описание процесса жидкофазного окисления толуола в его присутствии. Кинетическая модель жидкофазного окисления кислородом ароматических углеводородов, в присутствии нанокатализаторов на основе металлов переменной валентности, инкорпорированных в полимерную матрицу, позволит прогнозировать влияние участников реакции на скорость реакции и состав продуктов.

С помощью волюметрического, потенциометрического, спектрального и хроматографического методов проведено изучение кинетики жидкофазного окисления толуола кислородом в присутствии закрепленных на стекле инкорпорированных в полимерную матрицу полиэтиленимин-полиакриловая кислота $(\text{ПЭИ/ПАК})_n$ с различной толщиной (n) полислоев (от 10 до 40) комплексов меди (II), кобальта (II), железа (III), и совместно меди (II) и железа (III) при 348 К и атмосферном давлении.

Согласно данным ИК-спектрального и хроматографического анализов катализата продуктами реакции оксигенирования являются бензальдегид и гидропероксид толуола.

Из экспериментальных данных можно предположить механизм оксигенирования толуола в присутствии комплексов поливалентных металлов, закрепленных на (ПЭИ/ПАК), который включает образование и редокс-превращение промежуточного комплекса по стадиям (1) - (2).

$$[(\text{ПЭИ/ПАК})_n - \text{M}]^{m+} + \text{RH} \leftrightarrow [(\text{ПЭИ/ПАК})_n - \text{M (RH)}]^{m+} \tag{1}$$

$$[(\text{ПЭИ/ПАК})_n - \text{M (RH)}]^{m+} + \text{O}_2 \leftrightarrow [(\text{ПЭИ/ПАК})_n - \text{M (RH)(O}_2)]^{m+} \tag{2}$$

$$[(\text{ПЭИ/ПАК})_n - \text{M (RH)(O}_2)]^{m+} \xrightarrow{k} \text{ROOH} + [(\text{ПЭИ/ПАК})_n - \text{M}]^{m+} \tag{3}$$

$$\text{ROOH} \xrightarrow{kat} \text{RO} + \text{H}_2\text{O} \tag{4}$$

где M^{m+} - Cu^{2+}, Co^{2+}, Fe^{3+}, $\text{Cu}^{2+}/\text{Fe}^{3+}$; n – 30 полислоев.

В соответствии с перекисной теорией Баха молекула кислорода в обычном состоянии неактивна. Активация молекулы кислорода путем разрыва на отдельные атомы энергетически трудна. Значительно легче происходит разрыв одинарной связи –O–O–, чем двойной O=O. Такая активация происходит при оксигенировании легко реагирующих веществ, в результате которой образуются перекиси – первичные продукты этой реакции (3), которые разлагаются до альдегидов (кетонов) (4).

Введение в систему $[\text{стекло}/(\text{ПЭИ-ПАК})_n\ /\text{M}]^{m+}$ – RH – CH_3CN – O_2 тетрахлорметана, как инициатора процесса окисления углеводородов кислородом, приводит к увеличению скорости процесса и смене механизма на радикальный, в результате чего образуются$\cdot\text{CCl}_3$ и RCl, которые ведут процесс окисления.

XPS study of interaction between DNA and Cobalt Ferrite Nanoparticles: dry and wet-frozen samples comparison

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Nanobiotechnology is a complex of methods and approaches to designing nanostructures and the components of biological systems among them with specified properties. It is now the field of research of the most rapid development, because nanomaterials acquire unique physical properties due to surface and size effects. One of the prospective ways of nanobiotechnology is the design of hybrid bionanocomposites consisting of magnetic nanoparticles (MP) and nucleic acids (NA). Constructions on the basis of MP are used in genotherapy to develop nonviral vectors for drug delivery, in genodiagnostics to design selective sorbents for the isolation of NA. The second path of nanobiotechnology is the elaboration of nanobioelectronic devices and biosensors. The use of magnetic particles is attractive due to the possibility to detect them with high sensitivity and efficiently manipulate constructions on their basis by means of the application of an external magnetic field and the change of its force and direction. The small size of the particles is comparable with that of biomolecules, which allows for their specific interaction. The additional advantage of inorganic oxide ferromagnetic nanoparticles is their mechanical and chemical stability.

The interaction of NA and MP has, evidently, a complicated nature and can occur in different ways. The investigation of the interaction mechanisms plays a decisive role for the development of nanocomposite constructions. This knowledge determines the limitation of the use of the given construction, allows one to control the relations between its components, and opens the future prospect of the designing a surface which would provide for the high-specific binding of NA or prevent it. XPS is a one of efficient methods of the study which does not damage the sample structure and has a high sensitivity to the surface atoms layers. Thus the goal of present work was to study the interaction between DNA molecules and particles of ferromagnetic nanopowder $CoFe_2O_4$ using standard XPS technique as well as cryogenic XPS analysis of liquid samples.

The bionanocomposite samples were prepares through dG18, dT18 and dG18T25 oligonucleotides adsorption on the surface of $CoFe_2O_4$ nanoparticles. Aqueous, Tris and PBS-Tris buffer solutions were used. The standard XPS analysis of dried samples was taken on ES-300 KRATOS spectrometer equipped with AlK_α anode (1486.6 eV) with 196W power. Wet pastes and liquid solution samples were studied under cryo temperatures (-155 C) on AXIS Ultra standard electronic spectrometer (Kratos Analytical) with monochromated AlK_α excitation (1486.6 eV) with 180W power. To increase the intensity of the spectrum we used an additional magnetic lens to ensure an electron take-off angle of ±15° relative to the surface normal. The charging of the sample surface was compensated for by the use of a slow-electron gun. C1s. N1s, P2p, O1s lines were studied for oligonucleotides analysis, Fe2p, Co2p and O1s core-lines – for magnetic nanoparticles analysis.

For the entire range of samples the quota of adsorbed oligonucleotides was estimated. The comparison with XPS spectra of pure $CoFe_2O_4$ nanoparticles allowed to calculate the thickness of the adsorbed layer. The performed study of sample frozen in solution allowed to make conclusions about the conformational packing of the polymer on the surface of magnetic nanoparticles.

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Kinetics of selective acid-catalyzed deacetylation of fully acetylated phenolglycosides esters

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Natural glycosides with 2’-O-acetyl group are of great interest for medicinal chemistry, plant chemistry and phytochemistry [1, 2]; they also could serve as specific chemotaxonomic markers [3] for plants of *Salix* species. Despite the development of synthetic approaches in organic chemistry, 2’-O-glycosides have been obtained only by means of multi-step procedures involving different protective group strategy [4]. In our work, we suggested one-step acid-catalyzed hydrolysis procedure of fully-acetylated glycosides affording 2’-O-acetylderivatives in one step.

In the present study, kinetics of acid-catalyzed deacetylation of pentaacetyl salireposide [5] as illustrative example was investigated. Hydrolysis was monitored by HPLC and HPLS-ESI-MS analysis. According to HPLC analysis, two tetra-acetates, four tri-acetates, three di-acetates and only one monoacetate are formed simultaneously in the reaction mixture. That confirms that acid-catalyzed hydrolysis has complex nature.

Kinetics investigation at 16 °C showed that initial salireposide pentaacetate disappears during first hours of the reaction. Apparently, 6’-O-acetyl group and phenolic acetate are hydrolyzed primarily. At the same time, monoacetylated product quickly accumulates and reaches maximum concentration at 32 h, and slowly consumes after that. The fully deacetylated product forms slowly, moreover, after certain time (100 h) hydrolysis of benzoyl group is observed and salirepin is released via decomposition of deacetylated salreposide.

In order to determine optimal parameters of reaction, we performed acid-catalyzed hydrolysis at different temperatures: 16 °C, 30 °C and 50 °C. Thermodynamical characteristics were calculated assuming the acid-catalyzed hydrolysis as the first-order reaction. According to our calculations, reaction rate constants of acetyl and benzoyl groups differ by 6.6 times (0.2923 h^{-1} and 0.0444 h^{-1} respectively) at 30 °C. Whereas at 50 °C rates of all reactions are accelerated and rate constants are almost identical.

As a result, calculations revealed that optimal reaction time for reaction of acid-catalyzed glucopyranosides selective deacetylation is 3h for maximum concentration of 2’-O-acetyl derivative and 15h for fully deacetylated glycoside at 30 °C.

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SECTION 2:
Promising catalytic processes

New bicomponent massive sulfide catalysts in the reaction of dibenzothiophene hydrogenolysis

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An interest in massive hydrotreating catalysts is steadily increasing both in the Russia and abroad. This paper presents the results of a study of the catalytic activity of bicomponent catalytic systems synthesized by solid-phase method.

The composites were prepared by mechanochemical combination of commercial coarse-grained molybdenum disulfide (MoS_2) and micron sized Ni and Co powders in a vertical vibratory mill in an inert atmosphere. To determine an activity of the synthesized systems the experiments were performed in a ‘Autoclave Engineers Bolted Closure’ closed-type reactor with a total volume of 100 ml at a hydrogen pressure of 3.5 Mpa, a mixing rate of 600 rev/min, and a temperature of 340 °C. The volume of dibenzothiophene solution was 80 ml and its initial concentration was 500 ppm. The samples were taken out from the reactor one by one in 0.5, 1, 2, 3, 4, and 6 hours. The changes in the DBT concentration in intermediate samples were determined using UV spectroscopic method at the analytical wavelength λ_{max} = 324 nm. The analysis of the component composition of organic compounds in the samples was performed via gas chromatography-spectrometry (GC/MS) using a DFS magnetic mass spectrometer, ‘Thermo Scientific’ Co., Germany. The reactivities of the resulting catalysts were evaluated from the rate constants of dibenzothiophene hydrogenolysis and from the residual sulfur content in hydrodesulfurizates (OXFORD Instruments Lab. X 3500 SCL sulfur analyzer).

It is evident from the data of transmission electron microscopy (TEM), that the coarse-grained molybdenum disulfide is characterized by ordered crystal structure, so it represents long crystals, whose interplanar distance between the faces is 0.61 nm. The presence of amorphous molybdenum oxide on the MoS_2 surface is consistent with the data of technical certificate for commercial coarse molybdenum disulfide. In the course of mechanical activation of Co powder and molybdenum disulfide within 4 or 8 hours, the latter was subjected to nanofragmentation to form nanocrystallites packed from 3-6 structure units, which are about 10 nm long. The time of mechanical treatment increases from 4 to 8 hours, MoS_2 nanocrystallites retain their structural order, but they become increasingly curved and elongated.

It was found out that the maximum catalytic reactivity is exhibited by the catalytic systems prepared in the course of mechanical activation (MA) of 8 hours for component mixing ratios 1:7 and 1:10. Residual sulfur content serving the main criterion for their reactivities is 25 ppm. The respective rate constants of hydrogenolysis for the 8-hour MA are 0.7 and 0.6 h^{-1}, respectively.

In accordance with the available literature data, the reaction of dibenzothiophene hydrogenolysis might follow two paths with an equal probability – those of hydrating and cracking reactions, to form biphenyl and cyclohexylbenzene (via the formation of tetrahydrodibenzothiophene as an intermediate product of hydrogenation of dibenzothiophene), respectively. According to the chromatography-mass-spectrometry data for the latter two highly active catalysts, biphenyl and cyclohexylbenzene were observed in the reaction products, which implies that the hydrogenation followed the hydrating reaction path rather than that of cracking the C-S bonds in the heteroaromatic ring**.** In addition**,** the content in cyclohexylbenzene for the catalytic system with ratio 1:7 is twice higher than that for the comparative catalyst, which suggests that its hydrogenation ability is higher.

The results given suggest that alternative routing of hydrating or cracking reaction path is dependent on magnetic properties of the catalysts.

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Processing of the organochlorine waste on model Ni-M alloys by carbon erosion

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There is a dilemma between the increasing needs of the use of organochlorine compounds in all spheres of human activity and one of the most acute problems of modern ecology associated with the accumulation and disposal of their production waste. There are a number of both catalytic and non-catalytic methods developed for processing and utilization of organochlorine waste [1]. The authors of this work have focused on the development of catalytic method to utilize the multi-component mixtures of chlorinated hydrocarbons (CHCs). Decomposition of CHCs results in formation of nanostructured carbon material with unique properties thus extracting the carbon from the composition of waste [2].

The proposed method is based on the decomposition of chlorohydrocarbons on so-called self-assembled nickel (and Ni-M alloys) catalysts which can be formed *in situ* during the treatment of bulk metal precursors in the reaction medium. When being treated in aggressive reaction atmosphere at T = 500-700°C the bulk nickel alloys undergo disintegration which is driven by the phenomenon of carbon erosion. As a result, the complete destruction of Ni-precursors takes place thus giving the rise for dispersed nickel particles which catalyze the growth of submicron carbon filaments from chlorinated hydrocarbons. In the literature, this phenomenon is known as «metal dusting» [3]. The obtained self-organized catalytic system is characterized by enormously high activity and very stable behavior in aggressive media showing a huge performance for the carbon product (over 500 g/g_{Ni}) [4].

As it will be shown in the report, the developed approach to decomposition of chlorohydrocarbons into nanostructure carbon product has been successfully implemented not only for the model reactions, but also for utilization of the real waste of organochlorine synthesis provided by the chemical plant "Khimprom" (Volgograd, Russia). The massive binary alloys Ni_{1-x}-M_x (M = Co, Cu, Cr) synthesized by the coprecipitation and sintering method were used as catalyst precursors for the process [5]. It was found the carbon product is preferably formed as nanostructured filaments of submicron diameter. The morphology of the carbon filaments depends upon the reaction temperature at which a mixture of CHCs was decomposed, and characterized by very defective structure and high textural parameters.

In this paper we have also tested two different ways to supply the organochlorine waste into the experimental reactor. The first method consists in feeding to the reactor a gas carrier saturated with CHCs using the saturator. In the latter case, the waste is fed into the evaporator in the liquid state, from which they flow of the carrier gas delivered to the catalyst. It was established that the second approach allows one to avoid a change in the composition of the waste during the recycling process which leads to formation of more uniform carbon product.

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Synthesis by using plasma deposition of catalysts Pd/ZrO_2/stainless steel for combustion of organic admixtures and CO in auto exhaust

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The rise of automobiles quantities leads to rising of harmful organics and CO in cities air. For solving of this problem by catalytic combustion of these we have developed palladium catalysts on stainless steel grids.

The stainless steel grids were covered by plasma deposition by Al-Ni alloy as sublayer following by ZrO_2 plasma supporting. The ZrO_2 coating thickness is 80 – 100 mcm. Pd was supported by impregnation of prepared carrier by $Pd(NO_3)_2$ solution. Then samples were dried at 110 °C and then calcinated in air for 3 hours at 500 °C. The samples with Pd loading of 0,69%, 0,53%, 0,31%, 0,2 %, 0,06 % and 0,03 % by mass were prepared.

Catalysts activity in model reactions of CO and CH_4 complete oxidation was measured with use of flow installation and gas mixtures: 1 vol % of CO in air and 1 vol% of CH_4 in air. The contents of CO and CH_4 before and after reactor were measured chromatographically. The catalytic activity was determined as: 1. the temperature of reactions beginning; 2. the temperature of conversion X = 50% ($T_{50\%}$) of CO or CH_4; 3. the temperature of reaching the X = 99% ($T_{99\%}$).

The origin stainless steel covered by ZrO_2 begins is active in CO oxidation after 200^0C, but the CO conversion only 28% at 500^0C. $T_{50\%}$ of 0,03 % Pd catalyst is 197 °C, for 0,69 %Pd this value is 128 °C. For all catalysts X = 99% reaches in temperature interval 150 – 210 °C at residence time τ 0,3 - 0,5 s. Note that the light -off temperatures on these catalysts $T_l > 75^0$C.

The origin stainless steel covered by ZrO_2, begins to be active in the oxidation of CO at 200 °C. At 500 °C conversion of CO is 28 %. $T_{50\%}$ for the content of palladium 0,03 % of equal 197 °C, for 0,69 % - 128 °C. Conversion of CO at all catalysts reaches 99 % at the temperature of 150 - 210 °C at the time of contact 0.3 to 0.5 sec. Temperature of ignition on catalysts not below 75 °C.

The origin stainless steel covered by ZrO_2 don’t active in CH_4 oxidation in investigated temperature interval. The Pd catalysts are active beginning from Pd loading 0,2 % mass. $T_{50\%}$ for catalyst 0,2% Pd/ZrO_2/stainless steel is 495 °C, for 0,69% Pd the $T_{50\%}$ is 370^0C. For catalysts with Pd contents 0,69 %, 0,53 %, 0,31 % Pd the conversion X = 98% is reached in temperature interval 450 – 500 ^{0}C at τ = 0,5 s. The light - off temperatures in CH_4 oxidation on these catalysts $T_l > 250^0$C.

The received data allowed concluding that the catalysts Pd/ZrO_2/stainless steel prepared by using plasma deposition are perspective for combustion organics and CO in auto exhaust using the catalysts with Pd content $\geqq$ 0,2% by mass.

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Cr-containing catalysts for dehydrogenation of C_4-C_5 hydrocarbons in fixed-bed reactor

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Dehydrogenation of saturated hydrocarbons is a worldwide industrial method to produce olefins. The use of a fixed-bed catalyst makes this process both economically sound and profitable. Cr-containing catalysts are used in dehydrogenation of C_4-C_5 hydrocarbons due to their high activity and low costs. According to [1, 2] zirconia-supported Cr-containing catalysts are more active in dehydrogenation reaction than alumina and silica one, however, surface area of this materials is low. Hence, the development of new Cr-containing catalysts with different supports for dehydrogenation of paraffins to olefins is of vital importance.

The purpose of the present work is to study the effect of support properties on the state and activity of the active component (Cr_xO_y) in isobutane dehydrogenation. ZrO_2, SiO_2 and Al_2O_3 were used as supports. Cr-containing catalysts with loading of Cr corresponding to one monolayer were prepared by incipient wetness impregnation method using water solution of H_2CrO_4 and KNO_3 (K/Cr molar ratio was 1:5). The catalysts were dried at room temperature for 12 h and calcined at 500 ^oC for 4 h. The Cr loading was 1.5, 5.6 and 7.6 % wt. for Cr/ZrO_2, Cr/SiO_2 and Cr/Al_2O_3 catalysts, respectively. Catalysts were studied by low temperature N_2 sorption, TPR, UV-vis spectroscopy and tested in reaction of isobutane dehydrogenation in fixed bed reactor and kinetic conditions.

It was shown that states of chromium depended on the nature of support. The formation of large Cr_2O_3 particles was observed for Cr/SiO_2 catalyst. It causes low activity of this catalyst in reaction of isobutane dehydrogenation (Fig.1b).

Absence of reflexes of Cr-containing phases for Cr/ZrO_2 and Cr/Al_2O_3 catalysts in XRD patterns (Fig. 1a) indicates on small particle sizes (less than 3 nm) or covering distribution of chromia on the surface of these supports. Cr (VI) species were determined by TPR and UV-vis spectroscopy for Cr/ZrO_2 and Cr/Al_2O_3 catalysts. High activity of these catalysts was associated with formation of highly dispersed Cr_2O_3 due to reduction of Cr (VI) species. The highest activity of Cr/ZrO_2 catalysts may be explained by specific interaction of Cr with ZrO_2.

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Hydrogen production by hydrocarbons catalytic decomposition over Ni-Cu-Fe/Al_2O_3 catalyst as oil-well gas utilization technology

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Hydrogen is a highly effective and ecologically safe fuel that has numerous advantages over the currently used ones. It has great perspectives for wide application, especially as an automobile fuel. There are several well-known methods of hydrogen production. It's production by water electrolysis using various electrolytic cells is a well known and thoroughly studied process [1–3]. However, it requires a lot of electric energy. The oldest method still used for hydrogen production is coal gasification in the presence of water vapor at 800–900 °C. The resulting gas consists of 60% hydrogen mixed with CO and CO_2 [4]. Steam reforming of natural gas is the cheapest and most widely used in industry method for producing hydrogen [5,6]. Hydrogen produced by steam reforming has to be purified from carbon oxides that are poisons for the catalysts used for synthesis of ammonia, many hydrogenation catalysts and catalysts used in fuel cells. The costs of hydrogen purification increase the cost of obtained hydrogen [7].

The discovery of carbide cycle mechanism [8,9] makes it possible to develop a hydrogen production process where carbon nanofibers or nanotubes are produced instead of common soot. Different hydrocarbons can be used as the feedstock. For example, we used natural gas, propane-butane mix and gas mixture that simulate oil-well gas. The Ni-Cu-Fe/Al_2O_3 catalyst was prepared by mechanochemical activation of a mixture of transition metal oxides (Fe_2O_3, NiO, CuO) with aluminum hydroxide (hydrargillite) in a centrifuge planetary mill AGO-2 with cylinder rotation speed 10 s^{-1}. The total weight of the mixture was 5 g, and the total weight of crushing bodies was 200 g. During mechanical activation the mill cylinders were cooled with flowing water. If we used Ni-Cu-Fe/Al_2O_3 catalyst, we could get hydrogen and carbon nanofibers. The carbonization of the catalysts was performed in a flow quartz reactor. The reactor was equipped with a McBain microbalance, which allowed us to follow changes in the sample weight during the reaction and record the reaction kinetics. As was shown in [10], the optimum decomposition temperature of the catalyst is 700 ° C. The intensive thermal pyrolysis of propane-butane mixture was at 700 °C, but reaction products had only 10 % of hydrogen. However, bond breaking in propane and butane molecules occurred at 700 ° C and more simple molecules (as methane and C_2) were formed. It is important to note that among the major pyrolysis products present olefins (ethylene, propylene), which possess a high activity in the formation of carbon nanofilaments than saturated hydrocarbons. When we used Ni-Cu-Fe/Al_2O_3 catalyst in the propane-butane mix decomposition, we could obtain reaction products with 72 % of hydrogen. We suggest to used catalytic decomposition of hydrocarbon as a part of utilization oil-well gas and as ecologically safe hydrogen production technology.

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Characterization and catalytic activity of palladium supported on SiO_2, Al_2O_3 and ZrO_2

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Currently, in connection with environmental pollution and rise of operational requirements for gasoline, worldwide legislation about gasoline requires gasoline to possess high RON (research octane number), and to be eco-friendly. Therefore the role of processes making environmental components of gasoline is significantly increased. One of these processes is isomerization of C_5-C_6 alkanes. The isomerizate is free of benzene and other aromatic hydrocarbons, olefins, sulfur, nitrogen, and heavy metals, and that has the octane number from 83 to 92 RON depending on the process flow diagrams.

It is known that isomerization catalysts are bifunctional catalysts where the metal component is put on the acid support. As an acid component use Al_2O_3 and ZrO_2 modified by anionic additives, zeolites. Metal component of isomerization catalysts is Pt, Pd, Ni, Ir [1]. At the present time, in the industry use only platinum catalysts though systems Pd-containing too possess high isomerizing activity. Uniform idea of a role of a metal component in alkane isomerization reaction is not present, despite a large number of works in this area.

In our work, Pd/SiO_2, $Pd/\gamma\text{-}Al_2O_3$, $Pd/SO_4^{2-}/ZrO_2$ were prepared and studied, which differ with an electronic state of palladium. Also for more detailed research of state of Pd (oxidation level), physical mixtures Pd/SiO_2, $Pd/\gamma\text{-}Al_2O_3$ with SO^{2-}_4/ZrO_2 were investigated. X-ray diffraction analysis, temperature-programmed reduction, investigation of the textural characteristics of the catalysts was performed. Catalytic properties of catalysts were tested in n-hexane isomerization reaction. It is found, Pd/SiO_2, $Pd/\gamma\text{-}Al_2O_3$ are active in high-temperature range (340-500°C), and their mixtures with SO^{2-}_4/ZrO_2 are active in the range of lower temperatures (140-220°C). In work influence of an electronic state of palladium on catalytic properties is discussed.

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Development of enhanced corrosion resistant carbon supports for Pt/C catalysts for the oxygen electroreduction reaction

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End of XX - beginning of XXI century has been marked by an increased interest in alternative energy sources which include Proton exchange membrane fuel cell (PEMFC). This is due to the high efficiency of such devices, as well as environmentally friendliness (water as the only byproducts released).

It is known that during operation of the PEMFC as a power source for an electric vehicles the local value of the cathode potential can reach up to 1.5 V [1], which is much higher than potential of carbon oxidation. Therefore, the durability of the fuel cell is determined primarily by corrosion resistance of carbon support of the Pt/C catalyst in the oxygen electroreduction reaction (ORR). To investigate the corrosion resistance of catalysts an accelerated testing protocols ("Start-Stop cycling") in a standard three-electrode electrochemical cell was developed [2].

The present work aims to study the influence of the texture and pore structure of different carbon supports on the corrosion resistance of Pt/C catalysts.

Pt/C catalysts supported on Sibunit family of carbon materials were shown to have high corrosion resistance as well as high activity in the ORR [3, 4]. However, Sibunit-1562 support used in this work is characterized by the low specific surface area which is insufficient for high Pt dispersion. Therefore, to increase the specific surface area, Sibunit support was activated with air.

Pt/C catalysts based on KetjenBlack DJ-600 support are promising for use in PEMFC due to very high specific surface area. However, this material has low corrosion stability [5]. In this work, in order to increase the corrosion resistance of KetjenBlack DJ-600 sample, the C/C composite was synthesized by chemical vapour infiltration of carbon using the propane-butane mixture.

The results obtained were compared to commercial 40% Pt/Vulcan XC-72 and 50% Pt/TEC catalysts.

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Investigation of the pentasyl zeolites deactivation in the course of n-octane conversion

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An isomerization of pentane-hexane fraction is used in the industry for the production of environment-friendly high-octane gasoline components. The industrial processes for isomerization of C7 and above normal alkanes with the lowest octane number are currently not yet developed. The rapid deactivation of the available catalysts is one of the main reasons for this situation. Hence, the aim of this work is to prepare efficient catalysts based on pentasil zeolite and determine the time of their stable operation in the course of n-octane isomerization.

A high silica ZSM-5 zeolite with silica modulus 40 was prepared by hydrothermal synthesis and hexamethylene diamine was used as a structure-forming additive. Nanosized nickel powder (NSP) was obtained by gas-phase synthesis. Catalysts were prepared by mixing the zeolite powder and NSP in a KM-1 vibratory mill for 2 hours, followed by compressing the mixture into tablets, grinding, and sampling the 0.5-1.0 mm fraction to test. The NSP content in the catalyst was 0.5 wt%.

The degree of crystallinity for the synthesized zeolite and its belonging to the pentasyl family were determined by IR spectroscopy and X-ray analysis. The conversion of n-octane was carried out in a flow installation at a reaction temperature of 320 °C, a volumetric flow rate of 2 h^{-1} and atmospheric pressure. The duration of the catalyst operation was 16 hours, the reaction products were analyzed by gas chromatography every hour in the early stage of catalyst operation and every 2 hours later.

An investigation has shown that C4 - C8 alkanes and isoalkanes and alkylbenzenes are the main products of the n-octane isomerization over catalysts investigated. After the first hour of reaction over the initial H-ZSM-5 zeolite the yield of arenes was 15.7 wt.%, isoparaffins - 20.3 wt.%, naphthenes - 1.9 wt.%, alkenes - 3.8 wt.%, and conversion of n-octane reached 67.2 wt.%. The yield of these products over the modified catalyst sample was 9.3 wt.%, 32.8 wt.%, 2.6 wt.%, and 2.7 wt.%, respectively, and the conversion of n-octane was 89.4%. The degree of the n-octane conversion and the yield of reaction products decreased with increasing duration of the catalyst operation. The selectivity towards the formation of iso-alkanes over the initial zeolite reached its maximum value after 8 hours of the catalyst operation and then reduced. On the contrary, the selectivity towards a formation of iso-alkanes over the modified zeolite was minimal for this time of the reaction but then increased.

After 16 hours of the unmodified catalyst operation, the arene content in the reaction products dropped from 15.7 to 3.5%, that of isoalkanes - from 20.3 to 12.3%, and the conversion of n-octane decreased from 67.2 to 39.7%. A zeolite, modified with nickel NSP exhibited a more stable operation in the course of n-octane conversion as compared to the initial zeolite, which enhanced the formation of the iso-alkanes for 16 hours of operation on more than 10% while the conversion of n-octane decreased from 89.4 to 66.7 %.

Thus, the results obtained indicate a more stable operation of nickel-containing zeolite system as compared with the original sample, which is due to the presence of nickel-containing active sites in a catalyst system. These sites are involved in the reactions of hydrogenation-dehydrogenation resulting in a reduced rate of catalyst deactivation as compared to the initial zeolite.

Methanation of CO in the presence of CO_2 in hydrogen-containing mixtures on Ni- and Co/CeO_2

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Nowadays fuel cells with polymeric proton exchange membrane (PEM FC) are considered to be alternative and clean energy sources. Fuel for PEM FC is hydrogen. The H_2-rich gas 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 a method for purifying a hydrogen mixture [1].

Ni- and Co-containing catalysts are active in CO methanation. In this work we show the results on the comparative study of CO methanation in a realistic H_2-rich mixture on well-characterized (XRD, TEM, XPS, CO chemisorption) Ni- and Co/CeO_2 catalysts.

The Ni- and Co/CeO_2 catalysts were prepared by the incipient wetness impregnation technique. The CeO_2 support was impregnated by an aqueous solutions of chlorides and nitrates of nickel (II) and cobalt (II), then dried at 110°C for 2 h in air and reduced at 400 C for 2 h in the 5 vol.% H_2/He flow. Catalysts prepared from metal chlorides are designated as Ni(Cl)/CeO_2 and Co(Cl)/CeO_2, and from metal nitrates – Ni/CeO_2 and Co/CeO_2. The content of Ni and Co in the catalyst was about 10 wt.%.

The reaction was performed in a fixed-bed continuous-flow quartz reactor at atmospheric pressure. The experiments were performed with the following feed gas composition (vol.%): 1CO, 69 H2, 10 H2O, 20 CO_2 and at GHSV=29000 $sm^3g^{-1}h^{-1}$. The catalytic experiments were performed in the temperature interval of 180-360°C. The composition and concentration of the components of the gas phase was determined chromatographically. Progress of the reaction was characterized by concentrations of CO and CH_4 at the outlet of the reactor and the selectivity for CO.

Ni/CeO_2 and Co/CeO_2 have similar catalytic properties in CO methanation, and according to CO chemisorption, XRD and XPS they have a similar dispersion and structure. During the preparation of a metal chloride catalyst metal particles become larger and new phase Ce^{3+}OCl appears. Ni/CeO_2 and Co/CeO_2 are the most active in the CO methanation, but they also carry out CO_2 methanation. Co(Cl)/CeO_2 demonstrated no activity in the hydrogenation of carbon oxides, supposedly decoration of catalyst surface takes place. Only Ni(Cl)/CeO_2 catalyst provides selective methanation of CO in the realistic H_2-rich mixtures and decreases CO concentration to a level below 10 ppm. Apparently Ce^{3+}OCl phase inhibits the activation CO_2.

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Effect of ruthenium promotion on the reduction of Co-Al Fischer-Tropsch catalyst

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Cobalt-containing catalysts are generally supposed as the most efficient catalysts for the conversion of synthesis gas with high H_2:CO ratio to hydrocarbons. Highly active and selective catalysts should contain supported metallic particles with the preferable size of 6-10 nm. Stabilization of such a small particles over oxide support is a challenge, which demands the precise tuning of the strength of metal-support interaction. Various methods for the deposition of cobalt-containing precursors onto the oxide support and various combinations of the cobalt source and oxide composition were reported in literature. One of the promising methods is homogeneous deposition by precipitation of cobalt at urea decomposition conditions (DPU). Co-Al catalysts prepared by this method showed high activity and good selectivity in the Fischer-Tropsch synthesis [1]. However, the temperature of activation is high for these catalysts and exceeds 500^{o}C, which makes the reactor hardware and procedure expensive.

Introduction of tiny amount of noble metals helps decreasing the cobalt reduction temperature [2]. Noble metals serve as sites for activation of hydrogen and as nuclei for formation of metallic cobalt phase. Promoting metals also improves the activity of the catalyst. Unfortunately, Pt and Pd were shown significantly lower the selectivity of Co-containing catalysts to C_{5+} hydrocarbons and increase the yield of methane [3]. On contrary, Ru and Re were reported to improve both the activity and selectivity of the catalyst, prepared by impregnation of alumina and silica [3, 4].

Here we report the results on the effect of Ru promotion of Co-Al catalysts prepared by DPU method on their reduction behaviour in hydrogen. Ru was introduced by impregnation of freshly prepared or pre-calcined Co-Al catalyst with the solution of $RuNO(NH_3)_2(NO_3)_3$ complex. We have found that Ru promotion decreases the temperature of cobalt reduction and that the state of the catalyst prior to the impregnation with Ru strongly affects the scale of the reduction temperature shift. The reduction temperature dropped down to 310–350 ^{o}C, when Ru was introduced to the freshly prepared sample, which contained cobalt as the Co-Al double layered hydroxycompound. The reduction temperature shift was much smaller (down to 400–430 ^{o}C), when the catalyst was calcined before Ru impegnation and Co was mainly present as the Co-Al mixed oxide. It may be supposed that catalytic properties for these catalysts also differ. The study of the structure and catalytic properties of Ru-promoted catalysts are in progress.

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Membrane-catalytic dehydrogenation of ethane

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Nowadays, the needs for processing of natural and associated petroleum gases and their components are increasing; therefore petrochemists have to move from the inefficient gas flaring to its effective catalytic conversion into olefins.

Thus the creation of an efficient gas processing is of vital importance.

The catalytic dehydrogenation of light alkanes is an alternative method to the petrochemical production of olefins but it involves high temperature processing which requires both high power capacity and high capital costs.

The application of the membrane technology is one of the ways to solve the problem of high temperature dehydrogenation of alkenes into olefins. Significant attention has been recently focused on the application of membranes with selective permeability for hydrogen, including the processes of the simultaneous production of olefins [1].

It appears that the developing of ceramic membranes from carbon nanomaterials for the separation of the hydrogen from gas mixtures is very perspective.

Aluminosilicate ceramics membranes and some prototypes based on alumina using carbon nanotubes were manufactured in our research laboratory. Ceramic membranes with a pore diameter of 3-5 nm were obtained. Then physical and filter characteristics of obtained ceramics were analyzed. It is known that the maximum separation factor in the realization mechanism for the Knudsen diffusion for H_2-CH_4 mixture is $(mCH_4/mH_2)^{0.5} = 2.8$. However, one separation factor of the membrane towards hydrogen to H_2-CH_4 mixture was 3.

The developed ceramic membrane was cased into the reactor for ethane dehydrogenation reaction. The ethane dehydrogenation in a traditional reactor (without membrane), in a membrane reactor with membranes selectively permeable for hydrogen, and in a membrane-catalytic reactor with a fixed catalyst layer were compared under similar conditions. For comparison the process was carried out at various temperatures.

The membrane allowed the yield of ethylene to increase up to 1.8 times compared to the thermal dehydrogenation and up to 3.4 times compared to the use of Ce-Zr catalyst.

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Nanostructured Ag-containing catalyst for partial oxidation of diols to dialdehydes

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Partial oxidation of alcohols are important catalytic processes to produce valuable organic compounds such as aldehydes and acids. IB group metals are most active in these reactions and are used in industry to manufacture formaldehyde from methanol, glyoxal from ethylene glycol, etc. Polycrystalline Ag catalysts are the most effective ones. The problem of low stability and high cost of polycrystalline catalysts is not solved, and creation of new highly effective and stable catalysts is of vital importance today.

Development of nanostructured catalysts is an effective way to solve the problem mentioned, however, new concept should be suggested to stabilize silver nanoparticles in redox conditions and temperatures of 550-650 ^{o}C. The present work is devoted to synthesis of catalysts on the basis of support matrix, which has high thermal stability, suitable porous structure and function properties, needed to stabilize small silver particles.

The silica-phosphate phosphate matrixes were prepared by sol-gel technique [1] and impregnation method [2] and were used as support for Ag-containing catalysts. Silica was used as initial support due to wide porous structure and high thermal stability in redox condition. The phosphate component was used because of ability of reversible oxidation-reduction of silver in the presence of phosphate component in redox conditions [2], ability to stabilize small silver particles and clusters by phosphate [3].

It was shown that porous structure of catalysts may change in a wide range depending on conditions of sol-gel synthesis and variation of porosity of initial silica, when impregnation method is used to prepare the catalyst. The phosphate component is distributed mainly in pores of less than 10 nm and partially covers walls of pores with size of 10-60 nm. The $Ag/P_2O_5/SiO_2$ catalysts have specific surface area of 10-20 m^2/g and wide pores of 10-100 nm, which is favorable for high temperature catalytic process. It was shown by XRD that the presence of silver in silica-phosphate matrix implies crystallization of catalyst with formation of $Si_3(PO_4)_4$ and $Si_5(PO_4)_6O$ phases. Active component is stabilized in catalysts as metal silver nanoparticles (less than 50 nm with maximum of particles size distribution at 4-8 nm) and silver phosphate. The ratio of Ag/Ag_xPO_y depends on redox condition [4] and may be varied in catalytic process.

The catalytic activity of nanostructured $Ag/P_2O_5/SiO_2$ catalyst in reaction of ethylene glycol oxidation to glyoxal is higher than the one of polycrystalline Ag catalyst and Ag/SiO_2. Also, there are no carbon deposits on the surface of $Ag/P_2O_5/SiO_2$ catalysts because of small size of Ag particles and reversible oxidation-reduction of silver in redox conditions of catalytic process. The *in situ* IR-spectroscopy studies show that phosphate component participates in ethylene glycol adsorption, which changes the mechanism of alcohol transformation on the surface of silver particles [5]. Study of kinetics of ethylene glycol oxidation over $Ag/P_2O_5/SiO_2$ catalyst shows that conversion of ethylene glycol to glycol aldehyde and consequent transformation of glycol aldehyde to glyoxal takes place [5], while this route of ethylene glycol transformation over silver was considered to be negligible.

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Synthesis and photocatalytic properties of Cu- and Ni- modified $Cd_{0.3}Zn_{0.7}S$ for photocatalytic hydrogen production from aqueous solutions $Na_2S+Na_2SO_3$

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Conventional energy resources such as coal and petroleum products have been depleted to a great extent. It is therefore necessary to produce an alternative fuel, for example, hydrogen. One of the most perspective hydrogen production methods is photocatalytic water splitting with sacrificial agents such as Na_2S + Na_2SO_3. This donor system simulates process of photocatalytic decomposition of H_2S in alkaline solutions [1]. Earlier it was shown that the most active photocatalyst for hydrogen production from Na_2S + Na_2SO_3 solutions is $Cd_{0.3}Zn_{0.7}S$ [2]. In order the photocatalytic activity of sulfide materials may increase, it is doped by transition metals such as copper and nickel [3].

The Cu- and Ni-doped photocatalysts were prepared by such technique: salts of zinc, cadmium, copper or nickel with define molar ratios were mixed in a flask containing sodium hydroxide, and then sodium sulfide was added. The reaction system was stirred 20 min. Then the precipitate was centrifuged, washed and dried for 15 hours at 70°C.

The samples were characterized by XRD method. Ni-modified photocatalysts are solid solutions of cadmium, zink and nickel sulfides. Cu-modified photocatalysts consist of two phases - CuS and $Cd_{0.3}Zn_{0.7}S$. All samples were tested in photocatalytic hydrogen evolution from Na_2S + Na_2SO_3 aqueous solutions under visible light. Unfortunately, Ni-modified samples were inactive, perhaps, it was connected with more high position of Ni-donor level in the band structure of $Cd_{0.3}Zn_{0.7}S$. Cu-modified samples are more active than $Cd_{0.3}Zn_{0.7}S$, the maximum rate reaction is 0.204 µmol/min and is measured with using catalyst $0.01CuS\text{-}Cd_{0.3}Zn_{0.7}S$.

Other experiments were devoted by optimization of experimental conditions - Na_2S and Na_2SO_3 content, pH and catalyst's content. Kinetics experiments were shown that dependence rate reaction vs. sacrificial agents content was approximated by a such equation:

$$W = \frac{\alpha * C_{Na2S} + \beta * C_{Na2S} * C_{Na2SO3}}{\left(1 + K_{Na2S} * C_{Na2S} + K_{Na2SO3} * C_{Na2SO3}\right)^2},$$

where α and β are effective rate reaction constants ($\alpha = 4.4 \pm 0.5$ µl/min, $\beta = 170 \pm 43$ µl/(M*min)), K_{Na2S} and K_{Na2SO3} are adsorption constants ($K_{Na2S} = 7.8 \pm 0.7$ M^{-1}, $K_{Na2SO3} = 14 \pm 2$ M^{-1}). It has been noticed that this equation describes dependences of other researchers. Also we investigated dependence catalyst's content on rate reaction. Rate reaction linearly increases, goes through a maximum ($C_{kat} = 1.15$ g/l) and decreases because of reduction of light absorption. Then we measured pH dependence on rate reaction. It was observed that the increase of pH from 12.7 to 7.5 results in a substantial increase of reaction rate to 0.917 µmol/min. Further increase of solution pH to 14 results in decrease of the reaction rate because of thermodynamically process labored. If the pH values decrease, catalyst's decontamination can be realized because of elemental sulphur precipitation.

In conclusions, H_2 can be produced efficiently by photocatalytic splitting of water using Na_2S/Na_2SO_3 system as sacrificial agent and a solar light-simulating source. The best results were obtained for 0.01 CuS - $Cd_{0.3}Zn_{0.7}S$. The quantum efficiency was 23.7% that is a large value for a process on a catalyst containing no noble metal.

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Support modification for improving the performance of bimetallic NiPd catalyst in autothermal reforming of methane

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Natural gas is an under-utilized resource for liquid fuels and chemicals production. There are two major methods for methane processing: direct conversion to products and indirect conversion, most frequently, via synthesis gas. Autothermal reforming of methane (ATR of CH_4) is the most promising process for methane conversion to synthesis gas due to its high energetic efficiency and low susceptibility to carbon deposition [1,2]. As the ATR reaction occurs at 800–900°C, the specific role of catalyst support is to provide a high surface area and thermal stability, maintain dispersion of the metal particles and promote stability against sintering and carbon formation. This work is devoted to the study of the effect of support composition (CeO_2/Al_2O_3, ZrO_2/Al_2O_3, La_2O_3/Al_2O_3, $CeZrO_2/Al_2O_3$ and $La_2O_3/CeZrO_2/Al_2O_3$) on the nanostructure of bimetallic NiPd catalysts, and their performance in the ATR of CH_4.

The modification of Al_2O_3 support by CeO_2, ZrO_2, La_2O_3 or $CeZrO_2$ oxides was done by impregnation method, after that the active component precursors were loaded using co-impregnation method. The fresh and used bimetallic NiPd catalysts were characterized by N_2 adsorption, XRD, TEM, H_2-TPR and TG/DTA techniques. ATR experiments were performed in fixed-bed reactor with a feed composition of $CH_4/H_2O/O_2/He = 1/1/0.75/2.5$ and at temperatures 650-950^oC.

The characterization results exhibit that phase composition, NiO dispersion and Ni^{2+} reducibility are strongly affected by support composition. The increase of NiO particle size from 10 to 14 nm is observed at an increase of $CeZrO_2$ content from 0 to 30 wt.% in the $CeZrO_2/Al_2O_3$, while decrease of NiO particle size from 11 to 6 nm is found at an increase of La_2O_3 content from 0 to 20 wt.% in the $La_2O_3/10CeZrO_2/Al_2O_3$. The content of Ni-containing species reduced in high-temperature region (500-700^oC) increases with an increase of La content, which is connected with formation of La-Ni-O and Al-Ni-O species. The catalyst evolution under reaction conditions was studied. The high-temperature (850^oC vs. 500^oC) pre-calcination of support and absence of La in the catalyst composition allow keeping the S_{BET} value of used catalysts close to the initial level. The NiO (~15 nm) and NiPd alloy (~18 nm) phases were observed in the used catalysts. It was found that the Ni^o/NiO ratio can be regulated by support composition. The low-temperature calcination of catalyst (500^oC vs. 850^oC) and using the $10CeZrO_2/Al_2O_3$ support prevent the formation of carbon nanofibers.

It was shown that the prepared catalysts provided methane conversion of 90-100%, CO yield of 55-75% and H_2 yield of 55-70%. It was demonstrated that the catalyst performance changed at variation of support composition. H_2 yield increased with i) an increase of $CeZrO_2$ content from 10 to 20 wt.%; ii) an increase of La_2O_3 content from 5 to 20 wt.%. The optimal composition of catalyst was selected: at 850°C the $10Ni0.5Pd/20La_2O_3/10CeZrO_2/Al_2O_3$ catalyst provided the yields of 65% H_2 at CH_4 conversion 90-100% during a stability test that lasted 24 h. Correlation between catalytic and physical-chemical properties was established.

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Synthesis of copper-containing catalysts based on zirconium oxide and formation of active surface for ethanol dehydrogenation

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Conversion of alcohols (*bio* – alcohols) into valuable products and intermediates for fine chemistry is well-known processes. In recent years, it can be noted that interest in the use of environmentally friendly catalytic reactions, had been growing. These processes, for example, could replace the main method of acetaldehyde production via oxidation of ethylene, to avoid environmental pollution and a large number of wastewater [1–3].

The aim of this work was to study the physicochemical properties and catalytic activity of copper-containing catalysts based on zirconium dioxide. Zirconium dioxide was obtained via sol-gel method and stabilized with PVP (polyvinylpyrrolidone) [4]. After calcination procedures tetragonal ceramic ZrO_2 was obtained (DTA, XPA) and it was impregnated with copper chloride (II) with copper content 1, 3, 5 wt.%. All copper containing samples were reduced by H_2 at 400^0C. Catalytic experiments were performed on a flow-type setup with the chromatographic analysis of substances.

It is shown that the activity and selectivity of ethanol conversion depends on the pretreatments conditions, surface area, as well as on the loading of the catalysts. Activity of based ceramic zirconia dioxide was low [5]. Prereduction of copper-containing samples in a stream of hydrogen allows to produce acetaldehyde with 100% selectivity. Activity of reduced copper-containing samples depends on the copper content in the sample and correlated with the number of active surface sites. Moreover bond strength of alcohol with the surface decreases with increasing content of copper. Maximum conversion of ethanol in a dehydrogenation reaction reaches 60% at 380°C on reduced by H_2 copper-containing samples.

It has been investigated the possibility of activation of copper-containing nanocomposites based on zirconia dioxide using preliminary critical low-temperature treatments. Modifying the preparation process by adding low temperature quenching stage (T = –195°C) allows to achieve the most active catalyst with the 80% conversion of ethanol to acetaldehyde. Increased activity is connected with the formation of large number of active sites by creating additional defects of zirconia oxide and redistribution of copper ions on the surface before the reduction treatment.

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Methane activation study on Pt/Al_2O_3 in the perfect-mixing reactor

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After the oil crisis in the 70s of the XX century the mankind has turned to natural gas as alternative hydrocarbons source. Methane is a basic component of the natural gas mainly used as a fuel (≈5%). High strength CH-bond in a methane molecule is causing considerable difficulties when it is used in industrial processes. One of the most effective hydrocarbons activation methods is oxidation by oxygen or by active oxygen containing compounds.

Thus there are methane oxidation refining processes for producing of the synthesis gas to obtain oxygen containing compounds and synthetic oil in industrial scale. [1]. One-step methane oxidative condensation in C_2-hydrocarbons has been extensively studied [2]. However oxidation processes have a number of serious disadvantages, for instance, low desired products yield and unprofitability.

The second possible method of thermodynamic limitations overcoming by carrying out the reaction in two stages was described in beginning of the 90s in the XX century. At the first stage in the temperature range of 300–450 °C methane is chemisorbed followed by C-H-bond breaking and the formation of molecular hydrogen. C-C-bonds can be formed by reacting of neighboring species CH_x ($X \leq 3$) fragments. However, the resulting C_2-hydrocarbons precursors are strongly bounded to the catalyst surface and are not independently desorbed. To remove them from the surface to a gas phase there is a need to exposure in a hydrogen stream, usually at a lower temperature [3]. At present the process of methane chemisorption followed by activation and conversion to C_2-hydrocarbons is widely considered in the literature for the different oxide supported catalysts with a high metal content (4–10 wt%) mainly of VIII group.

In the present work a technique of the methane activation study in the perfect-mixing reactor was developed and $Pt/\gamma\text{-}Al_2O_3$ catalyst was studied. The catalyst was prepared according to the standard procedure for reforming catalysts. Pt loading was 1 wt %. The catalyst was reduced in hydrogen flow at 500 °C for 1 h prior the reaction. CH_4 was fed to the catalyst up to $Pt:CH_4$ ratio equal 1:20 mol/mol. Methane was absorbed on the catalyst surface in the temperature range of 20–550 °C. To investigation the reactivity of CH_x-species chemisorbed on the catalysts surface at 550 °C n-pentane was introduced to the reaction mixture up to $CH_4:C_5H_{12}$ ratio equal 1:2 mol/mol. Argon was used as an internal standard for the methane conversion calculating.

It was found that methane begin to adsorb on the catalyst surface at 400 °C by dissociative mechanism. The proof of this is the hydrogen appearance and the CH_x-species formation on the catalyst surface. Maximum of methane adsorption is observed at 550 °C. It is equal 1:1,7 $Pt:CH_4$ ratio. If reaction temperature increase the CH_x-species dehydrogenation degree increases ($CH_4 – CH_3 – CH_2 – CH - C$).

In the perfect-mixing reactor n-pentane is cracking in the presence of a $Pt/\gamma\text{-}Al_2O_3$ catalyst at a temperature of 550 °C mainly to gaseous hydrocarbons. At first it was found that n-pentane injection in a reactive system containing CH_x species on the catalyst surface results in the formation of aromatic hydrocarbons in a significant amount (up to 18 mol%). This phenomenon may be related to coordinating interaction n-pentane with CH_x species on the catalyst active sites.

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Catalysts Cu-Zn-Al-O for oxidative desulfurization DBT in model diesel fuel

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During the last decade the requirements to the limits of sulfur content in motor fuels have been constantly toughened. In accordance with the current emission standard EURO-V the content of sulfur in diesel fuel should not exceed 10 mg/kg (10 ppmw). The sulfur removal from oil is, consequently, one of the cardinal problems in most refineries. The cost of a crude oil processing is influenced by its sulfur content and by technology used for the sulfur-free oil production [1].

The concentration and nature of the sulfur-containing compounds in crude oil have been found to change over the boiling range. The amount of sulfur in a distillation fraction increases with an increase in boiling range, with the heaviest fraction containing the most sulfur [1]. The sulfur compounds become more hydrodesulfurization-refractory with increasing boiling point, as the dominant compound class changes from thiols, sulfides, and thiophene in the naphtha to substituted benzothiophenic compounds in the distillate [2]. In the vacuum gas oil and vacuum residue, the sulfur is contained mainly in compounds of the dibenzothiophene family. One of promising method for diesel fuels desulfurization is selective oxidation of their sulfur-containing compounds over catalysts with oxygen. Therein during this process the sulfide and heterocyclic sulfur-compound are transformed to sulfur dioxide, and the hydrocarbon fragment is oxidized to carbon dioxide and water [1].

The aim of this work is to study the physicochemical properties of Cu-Zn-Al catalysts and determination of their activity in the oxidative desulfurization of model fuel (DBT-Toluene, 0.1-0.5 wt.% S) and diesel fuel (1 wt.% S). Cu-Zn-Al catalysts were prepared by the precipitation, the their copper loading are ranged from 10 to 45 wt.%. The ODS tests were conducted in the temperature range 250-430^oC at a ratio of $O_2/S = 120$, GHSW = 3000 h^{-1} and WHSW = 6 h^{-1}.

XRD study has showed that the 10 wt.%Cu-Zn-Al catalyst contains an amorphous phase. Increasing the copper concentration to 25-45 wt.% leads to the crystallization of CuO and ZnO phases. According to TPR-H_2 results the Cu-Zn-Al catalysts are reduced by hydrogen in a single step at a temperature of 200-300^oC, and are characterized by the ratio $H_2/Cu = 0.85-1.05$. Comparison with literature allows us to conclude that the copper is the Cu(II) state and likely located in CuO and $CuAl_2O_4$.

The main ODS reaction products are sulfur dioxide, carbon dioxide, water and desulfurized fuels. The catalyst with a copper content of 10 wt.% is not active in the DBT conversion in the temperature range 250-430^oC. Increasing copper content to 25-45 wt.% results in a rise of the oxidative desulfurization activity, and the DBT conversion is observed at temperatures 350^oC and above. The catalyst with 45 wt.% of Cu exhibits the maximum conversion of DBT to SO_2 equaled to 45% at temperatures of 350-400^oC and the sulfur removal from the diesel fuel is about 40%.

The method of CHNS analysis found that spend catalysts have sulfur and carbon accumulated on the catalyst surface in an amount of 5±0.5% C and 1.8±0.2% S. XRD data are recorded the particle Cu_2O and Cu^0 formation. DTA-TG-MS analysis shows that the sulfur on the catalyst surface is represented by the sulfides/polysulfides and sulfate of metals, which is decomposed at 100-300°C and 700-850°C, respectively. Carbon deposition is products of the hydrocarbon condensation, they oxidized into CO_2 and H_2O at 350-450^oC.

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Hydrodeoxygenation of methyl palmitate and rape oil over silica-supported molybdenum phosphide catalysts

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Transition metal phosphides are considered as promising materials for hydrodeoxygenation (HDO) of renewable feedstocks such as vegetable oil and bio-oil [1,2]. These catalysts are an alternative in the HDO to conventional hydrotreating sulfide systems (NiMoS/γ-Al_2O_3 and CoMoS/γ-Al_2O_3) and supported precious metal catalysts, as the sulfide catalysts suffer from deactivation in absence of sulfiding agent and precious metals are high-priced.

The aim of the present work is study of the silica-supported molybdenum phosphide catalysts in the HDO of a vegetable oil model compound – methyl palmitate ($C_{15}H_{31}COOCH_3$) and in the HDO of a real feedstock – rape oil.

The catalysts were prepared by the impregnation of silica with aqueous solutions of ammonium paramolybdate $(NH_4)_6Mo_7O_{24}$ and ammonium hydrophosphate $(NH_4)_2HPO_4$ (A-method) or phosphorous acid H_3PO_3 (I-method), followed by drying, calcination and reduction in hydrogen flow. The catalysts were characterized by elemental analysis, N_2 physisorption, H_2-TPR, XRD, HR-TEM and XPS. The catalytic activity was evaluated using fixed-bed continuous-flow stainless steel reactor at 290-350°C, 3.0-5.0 MPa.

According to the XRD data in case of both (A) and (I) methods molybdenum phosphide was amorphous on the surface of the SiO_2. HR-TEM data showed almost the same particles sizes in the (A) and (I) samples (1.4-2.0 nm). XPS analysis confirmed the same Mo:P ratio on the surface of the SiO_2 before and after reduction.

Molybdenum phosphide catalysts performed high catalytic activity in HDO of methyl palmitate. The activities of (A) and (I) samples were almost identical. Yield of hydrocarbons at 290°C was about 90%. It was found that HDO of methyl palmitate over molybdenum phosphide catalysts goes mainly through H_2O and C_{16} hydrocarbons formation (~97%).

Rape oil contains generally triglycerides of unsaturated C_{18} fatty acids (oleic 62.8%, linoleic 20.3%, linolenic 7.6%). HDO of rape oil over molybdenum phosphide catalysts goes mainly through H_2O and C_{18} hydrocarbons formation.

In conclusion, phosphorous precursor did not influence on physico-chemical properties, activity and selectivity of MoP/SiO_2 in HDO of methyl palmitate and HDO of rape oil. MoP/SiO_2 showed high stability during 70 hours HDO of rape oil.

The work was performed in the framework of the joint Research and Educational Center for Energoefficient Catalysis (Novosibirsk State University, Boreskov Institute of Catalysis).

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n-Heptane isomerization over Pt/WO3/ZrO2 for environmental fuels production

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Nowadays environmental protection regulations are becoming more stringent for automotive fuels. As aromatic hydrocarbons content of classes 4 and 5 must not exceed more than 35 vol % (including benzene less than 1 vol %) [1], it is necessary to reduce the fraction of aromatics. One possible way of aromatics content reduction is C_7-fraction isomerization (70–105 °C), selected from gasoline fraction with final boiling point 180 °C. It will diminish aromatics content in gasoline and keep the high octane number. At present there is no C_7-fraction isomerization in industry, but it is very important process for refining industry.

Catalysts for n-heptane isomerization should have less acidity compared with catalysts for C_5-C_6-fraction isomerization due to n-heptane molecule is more easily cracked [2]. Among all catalysts for n-heptane isomerization the catalysts based on tungstated zirconia dioxide are most effective for this process [3]. According to data [4] different catalyst preparative variables affect the catalytic properties. At present work $Pt/WO_3/ZrO_2$ catalysts with different WO_3 loadings were prepared and studied.

$Pt/WO_3/ZrO_2$ catalysts were prepared as follows. Hydrous zirconia was precipitated from zirconium sulfate with aqueous ammonia solution under vigorous stirring and pH 9–10. The samples of WO_3/ZrO_2 were prepared by impregnation of hydrous zirconia with aqueous solution of ammonium metatungstate followed by calcination. The WO_3 loading was varied in the range of 10–25 wt %. Pt was loaded at 1 wt % on the WO_3/ZrO_2 with aqueous solution of H_2PtCl_6 followed by calcination in dry air flow at 450 °C.

IR-spectroscopy, X-Ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM) studies of prepared samples were conducted. According to IR-spectroscopy data with tungsten oxide loading increasing the Bronsted acidity increase. With XRD-study we examined the ratio of the tetragonal and monoclinic phases of ZrO_2. Platinum localization and particles size were determined with HRTEM.

Catalytic tests data showed the following activity dependence: Pt/10WZ < Pt/15WZ < Pt/25WZ, where 10–25 – wt % of WO_3 loading, W – WO_3, Z – ZrO_2. The best catalytic properties were achieved over catalyst with WO_3 loading 25 wt % at 170 °C: conversion – 83 %, liquid hydrocarbons yield – 85 wt % and multi branched isomers yield – 22 wt %. Recycle of n-heptane and methyl-hexanes will provide a higher yield of the multi branched isomers, which may be involved in production of environmental fuels containing less aromatics and having the high octane number.

IR-spectroscopy and HRTEM were performed on the base of equipment of Boreskov Institute of Catalysis SB RAS.

XRD and textural properties were determined on the base of equipment of Omsk Research Collaboration Centre SB RAS.

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Ni-containing spinel catalysts MnxCr3-xO4 for steam reforming of ethanol

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In the last years biomass has been recognized as one of the major world renewable energy sources. Transformation of biofuels derived from the fast pyrolysis of biomass or bio-ethanol into syngas is one of the most important tasks of catalysis in the energy-related fields. [1]

This work presents experimental results of the catalytic properties of spinel-type oxides $(Mn,Cr)_3O_4$ promoted by Ru +Ni in ethanol steam reforming (ESR).

Spinel-like mixed oxides $Mn_xCr_{3-x}O_4$ (x=0.3-2.7) were prepared via modified Pechini route [2] and calcined at 500 °C for 2 h. Ni or Ru (2 wt.%) were supported on oxides by the incipient wetness impregnation with $Ni(NO_3)_2$ or $RuCl_3$ solutions followed by drying and calcinations at 500°C for 2 h.

Samples were characterized by BET, XRD, UV-Vis, SEM, XPS, H_2 TPR. The catalytic properties of these samples in ESR were studied in diluted (0.5% C_2H_5OH+ 2% H_2O in He, contact time 18-54 ms) and concentrated (10% C_2H_5OH+ 40% H_2O in He, contact time 70 ms) feeds.

According to XRD and UV-Vis data, as-prepared samples are comprised of several phases. Samples with a high Cr content contain cubic spinel $MnCr_2O_4$ and hexagonal Cr_2O_3. In samples with a high content of Mn phases of tetragonal Mn_3O_4 and cubic Mn_2O_3 are observed. Due to a low content of supported Ni and Ru and their strong interaction with oxides, they are not detected as separate phases.

According to H_2 TPR data, for all samples with supported Ru reduction of catalyst begins at lower temperatures than for unpromoted oxides. In the same time no TPR peaks of reduction of RuO_2 were observed, that confirms strong interaction between oxides and supported metals.

A high-resolution image shows nanocrystalline particles of chromium-manganese spinel with sizes up to 10 nm. However, there are also large well-crystallized spinel particles. In fresh sample no individual particles of RuO_2 or NiO are observed, however, nickel and ruthenium are present according to EDX. They may be incorporated into the surface layers. In reaction conditions, nickel and ruthenium segregate to the surface forming metal alloy particles with sizes 2- 10 nm strongly interacting with support.

All catalysts demonstrated a high efficiency and stability in the reaction of steam reforming. Sample 2%Ru+2Ni%/$MnCr_2O_4$ showed the best results. In dilute feeds evolution of hydrogen begins at 300°C and attained maximum - 2.5% - at 600°C. In concentrate feed hydrogen yield was 33% at 700 °C and ethanol conversion was complete at 600 °C. As by-products, methane and small (<1%) amounts of ethylene and acetaldehyde were observed at low temperatures. These results are better than previously obtained for fluorite and perovskite based catalysts earlier investigated in similar conditions in ESR [3].

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Surface modification of microfibrous materials via cabon nano filaments

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Polymer composites based on microfibrous materials are of a great importance nowadays. Such composite materials possess high strength and low weight [1].The most promising microfibrous materials are carbon microfiber, glass fiber and basalt fiber. It is known that glass fiber is the typical reinforcing material for polymer composites. Carbon fiber is used when there are more specific requirements (e.g., space technology, the aircraft industry, military applications and sports). Also the world production of polymer materials reinforced with microfibers amounts 43 thousand tons per year. Basalt fiber is natural analog of glass fiber, its reinforcement abilities now is poorly investigated [2].

It is well accepted that the surface of mircoribers needs to be modified due to low adhesion level between fiber and polymer matrix [2, 3]. Adhesion level is believed to be improved with increasing surface area of pristine fiber. There are different chemical and physical modification techniques. For example, acidic treatment or plasma polymerization techniques are used to modify glass and basalt fiber [3]. Also catalytic chemical vapor deposition (CCVD) method is quite popular for carbon microfiber modification with nanostructured carbon [4].

In terms of research, composite samples x % CNF/MF were synthesized (x – wt. % CNF, ranged from 1 to 200%). In this work different types of microfibrous material (namely carbon fiber, glass fabrics and basalt fiber) were used.

All samples were prepared by unique technique. Nanostructuring of microfiber surface was carried out by CCVD of 1,2-dichlorethane in vertical quartz tube reactor [5]. Catalytic particles of nickel were deposited via impregnation or combustion technique. In the first case impregnation was followed by drying and reduction in hydrogen flow. In the second case there was no drying. It should be noted that 1,2-dichlorethane is the component of the wastes from vinylchloride manufacture and its utilization is known to be very challenging process since 1,2-dichlorethane is very hazardous and toxic. Thus aforementioned method enables one to modify fiber samples using technique advantageous from ecological and economical point of view.

The CNF/MF samples obtained were characterized using scanning and transmission electron microscopy. It is worth mention that the developed method allows us to obtain composites CNF/MF with feathery structure of carbon nanofiber. In some samples secondary disintegration of catalyst particles was observed.

It was shown that the method suggested is useful for modifying different types of microfibrous material (carbon fiber, glass fabrics and basalt fiber)

Using the BET method it was shown that surface area increased up to ten times after modification. In other words, modification results in increasing of surface area from 1.8 to 6-20 m^2/g which makes CNF/MF materials to be promising in the reinforcement applications.

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Effect of support pretreatments on catalytic activity and stability of silica-supported titania catalysts in H_2O_2-based oxidation of 2,3,6-trimetylphenol to trimethyl-p-benzoquinone

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Trimethyl-p-benzoquinone (TMBQ) is a key intermediate in the synthesis of vitamin E. Nowadays, there is a strong demand for the development of efficient and environmentally benign catalytic systems for TMBQ production. Silica-supported Ti dimers or small oligomers are known as highly active and selective catalysts for oxidation of alkylphenols to benzoquinones with the green oxidant – aqueous hydrogen peroxide [1]. However, there is no balance yet between high activity and stability of such catalysts. To solve this problem, we investigated the effect of silica pretreatment, which influences on the hydroxyl coverage of the surface, on catalytic properties and stability of silica-supported titania catalysts. The initial silica support was obtained by sol-gel method [2] and calcined at 600°C in air (support 1, SBET = 235 m2/g, Vpore = 0.77 cm3/g, and Daver. = 12.6 nm). Then it was subjected to hydrothermal treatment in the presence of ammonia to rehydrate partially the silica surface and dried at 100 oC (support 2). Alternatively, support 1 was kept under vacuum for 20 min at 80°C and for 40 min at 100°C (support 3). Three catalyst samples have been prepared by grafting titanium isopropoxide onto the three silica supports in dry toluene. The samples were characterized by elemental analysis, nitrogen adsorption measurements, DRS UV-vis and Raman spectroscopy. According to the spectroscopic techniques, the catalysts contained small titania clusters supported on mesoporous silica. The pretreatments did not change essentially the textural properties of the catalysts and the titanium state.

Catalysts 1–3 were tested in oxidation of 2,3,6-trimethylphenol to 2,3,5-trimethyl-1,4-benzoquinone with 30% H2O2. The reactions were initiated by addition of 0.35 mmol H2O2 to a mixture, containing 0.1 mmol of TMP, 14 mg of catalyst, internal standard (biphenyl), and 1 mL of anhydrous CH3CN. The results showed that the mode of the support pretreatment strongly affects both the catalytic activity (1 < 2 < 3) and selectivity towards the target product, TMBQ (1 ~ 3 > 2). Therefore, only catalyst 3 revealed a blend of high activity and high selectivity. Over it, TMBQ selectivity attained 93% at 90% substrate conversion after 35 min. Catalyst 3 also demonstrated better recycling performance than catalysts 1 and 2. No decrease of TMBQ selectivity and TMP conversion was observed after three reuses. Although the reaction rate partially decreased after the first use, it stabilized in the next runs. Hot catalyst filtration test confirmed true heterogeneous nature of the catalysis, while elemental analysis of the filtrate collected after the reaction showed no titanium leaching into solution. We suppose that the observed differences in the catalytic activity and stability of catalysts 1–3 could be due to different amount of SiOH groups on their surfaces and/or the size of TiO_2 clusters. Further work is in progress to clarify this matter.

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Oxidative coupling of methane over promoted MnNaW/SiO_2 catalysts

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Design of highly efficient catalysts for direct conversion of methane will solve such problems as rational utilization of natural gas and environmental protection [1]. The production of C_2 hydrocarbons (i.e. ethylene + ethane) through the oxidative coupling of methane (OCM) is an attractive direct way of the natural gas utilization into value added products. The MnNaW/SiO_2 type materials are most effective catalysts for OCM [2], and therefore we have undertaken a systematic synthesis, physicochemical and catalytic characterization study of a series of such compositions and their modifications. These studies will be applied to understand the structure-property-performance relationships and elucidate crucial factors, variation of which at the stage of catalyst preparation will allow regulation of the OCM reaction parameters.

For the preparation of MnNaW-based catalysts the commercial Silica gel Davisil 646 was used. The MnNaW/SiO_2 catalysts were prepared by incipient wetness impregnation using appropriate metal salts as precursors. The modification of MnNaW/SiO_2 catalyst by Ce, La, Zr, Cl, P or S was performed at variation of additive content. The characterization of the properties of prepared catalysts was performed by N_2 adsorption, XRD, TEM and XPS techniques. OCM experiments were performed in a fixed-bed reactor with a feed composition of $CH_4/O_2/He = 4/1/2$ at temperatures 700-900^oC.

It was established that at introduction of promoters (La, Ce, Zr, P, Cl) phases which are observed in non-modified samples (α-cristobalite, tridymite, Na_2WO_4 and Mn_2O_3) generally remained and formation of additional phases was also observed (for example, La_2O_3; Na_3PO_4). In case of S additive, the disappearance of Na_2WO_4 phase was found. According to TEM data, for non-modified MnNaW/SiO_2 catalyst two kinds of particles on the surface of SiO_2 support were found: with high (1-2 nm) and rough (up to 50-100 nm) dispersion. The composition of particles of high dispersion is very variable and all supported metals (Mn, W and Na) are present in their composition. The particles of rough dispersion have good cristallinity and different composition ($(Mn_2O_3)_3MnSiO_3$, MnO_x, WO_x/Na_2WO_4). The La introduction leads to formation of bimetallic oxide particles (La-Mn-O, La-W-O) with 50-500 nm size.

It was shown that the C_2 product yield in the OCM reaction over MnNaW-X/SiO_2 catalysts was strongly affected by the type and content of the promoter X (X = La, Ce, Zr, S, P, Cl). Among all promoters only Cl introduction leads to the notable improvement of catalyst performance and shifts the maximum of C_2 yield to low-temperature region (750^oC vs. 850^oC). The modification of MnNaW/SiO_2 sample by La (2-5 wt.%) or Ce (2 wt.%) slightly influences the activity but improves the stability of catalyst during the durability test in the OCM reaction. On the contrary, at modification by Zr (0.3-3.3 wt.%) catalyst performance goes down: at 850^oC the methane conversion and C_2 yield decrease from 35 to 6-30% and from 15 to 2-10%, respectively. The S or P introduction also leads to a considerable decrease of both C_2 yield and C_2 selectivity - generally at the expense of a decrease of C_2H_4 formation. The optimal composition of the catalyst was selected: the 2Mn1.6Na3.1W-2La/SiO_2 provides C_2 hydrocarbons yield of 22% at 54% methane conversion and 800^oC.

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Synthesis and properties of plasma dynamically prepared titania-based photocatalysts

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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, nontoxicity and relatively low price [1]. The photocatalytic activity of main modifications of titania, namely rutile, brookite and anatase, is the highest for the latter with the band gap of 3,2 eV [2]. Searching for new techniques of titania preparation provides the opportunity to achieve unique semiconductor properties.

In the following study samples of titania were prepared by the plasma dynamic technique [3]. The synthesis was carried in the coaxial magneto-plasma accelerator. The flow of the impulse hypersonic stream was conducted in the atmosphere of air in the isolated reactor chamber. The quantity of transfer energy W_m has been changed in experiments.

A model reaction of methylene blue photodegradation was taken as a method of the photocatalytic activity evaluation under UV-Vis irradiation with the use of Xe lamp.

XRD method has shown the presence of both rutile and anatase phases in the prepared samples as well as some amount of titanium nitride resulted from an interaction with the atmospheric nitrogen. The study of the particle size distribution has revealed that the general particle size does not exceed 70 nm and their shape proved to be spherical. UV-Vis spectra demonstrate a considerable shift of the light adsorption zone to the visible area which also might be due to the presence of titanium nitride.

The testing reaction has shown the considerable increase of the photocatalytic activity for all samples in comparison with model catalysts TiO_2 Degussa P25. The increase of the photodegradation rate constant might be due to the presence of titanium nitride in all studied objects as well. Sample 1 possesses the highest constant value in the initial stage of the experiment, while the lowest methylene blue concentration is reached for the sample 2, containing the biggest amount of titanium nitride – 7,1%.

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Heterogeneous catalysts in CL-20 syntesis

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Industrial synthesis of high energy product 2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-Hexaazaisowurzitane (CL-20) includes two successive stages of substituting hydrogenolysis. Hydrogenation in presence of acetic anhydride gives the formation of 4,10-Dibenzyl-2,4,8,12-Tetraacetyl-2,4,6,8,10,12-Hexaazaisowurzitane (DB). The second stage of the hydrogenation of DB up to 4,10-diformyl-2,4,8,12- Tetraacetyl-2,4,6,8,10,12-Hexaazaisowurzitane (DF) is carried out in the solutions of formic acid.

Heterogeneous catalyst of hydrogenolysis of Hexabenzylhexaazaisowurzitane (GB), with Sibunit being used as a support for 6% palladium (Pd), partially loses is activity during reactions after several cycles of its use and is subject to processing. Complete catalyst processing is a very power and labourconsuming process, when not only some Pd part is lost irrevocably but Sibunit support burns completely. Thus, apart from multiple catalyst application there arises the problem about replacing Sibunit support for the one that would not burn on processing and in consequence could be used when applying Palladium. The solution of this problem is focused on significant reduction in the cost of final product CL-20 [1].

Pd catalysts on oxide supports are widely used in chemical industry that is caused by a set of their properties, first of all, their stability at work and possibility of relatively easy regeneration.

The catalyst based on inorganic support γ-Al_2O_3 has been selected as an object for investigation. Only 1% Pyrocarbon burns during its processing that makes it possible to reduse demand in raw material during the repeated production of the catalyst comared with the Subunit support.

Series of tests on this catalyst showed that at the first stage of debenzylalion the larger part of calculated Hydrogen amount (about 90%) is absorbed for the first several minutes of reaction (at pressure 10 atm) and the rest (about 10%) for 1-2 hrs. The optimal time of reaction has been found to be 2 hrs. Increase in time does not cause the increase in yield, as the reaction finishes when absorption of Hydrogen stops. At present palladium catalyst on Carbon support is being used at the stage of reduction debenzylation[2] .

Hence, it can be concluded that the application of catalyst on γ-Al_2O_3 makes it possible to save support significantly and to use it multiply without essential losses, and also reduce the reaction time largely. This will give a significant cost reduction of the final product CL-20.

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One-step process of N-methylaniline production

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N-methylaniline is widely used as basic raw material for organic synthesis in chemical and pharmaceutical industries, as additive in paint and varnish industry as well as a component of high-performance antiknock additive to petrol fuels [1]. Nowadays N-methylaniline is produced by two-step process: hydrogenation of nitrobenzene with molecular hydrogen followed by alkylation of aniline with methanol. Both processes can be carried out under similar conditions on the same catalytic systems. Therefore this study was aimed at the development of new one-step environmentally friendly process of N-methylaniline production from nitrobenzene and methanol using bifunctional heterogeneous catalysts.

Different metals supported on alumina were used as catalysts. All catalytic materials obtained were characterized using low temperature adsorption-desorption of N_2, temperature-programmed desorption of NH_3, temperature-programmed reduction by H_2 and chemical analysis. Catalytic experiments were carried out in fixed-bed flow-type reactor under atmospheric pressure. At the first step, the most appropriate metal component responsible for selective hydrogenation of NO_2 group was selected. A series of catalysts, involving different metals (copper, nickel, silver, palladium and platinum) supported on alumina, were tested in the reduction of nitrobenzene. The results pointed that VIII group metals (Pt, Pd, Ni) give many by-products at high nitrobenzene conversions, silver proved to be more selective, but unstable with time-on-stream only 2 hours, thus copper showed the highest activity, stability and selectivity and was chosen as hydrogenating component of the catalyst.

At the second step, copper-containing catalysts were modified with different metal oxides (oxides of Fe, Mn, Cr, La, Zn) and investigated in hydroalkylation of nitrobenzene with methanol. The addition of chromium, manganese and iron had positive effect on the catalyst's performance: both nitrobenzene conversion and N-methylaniline selectivity increased. This improvement could be explained by higher acidity, evidenced by TPD of ammonia. On the other hand, addition of zinc and lanthanum had negative effect on the catalyst activity owing to the decrease in acidity.

At the final step of the study, the effect of the reaction conditions including temperature, weight hourly space velocity (WHSV), molar ratio methanol/nitrobenzene and hydrogen/nitrobenzene on the activity and selectivity has been investigated. The experiments were carried out over the catalyst, containing 7,5 wt.% Cu and 5,0 wt.% Cr supported on alumina. The best catalytic performance was obtained in the temperature range of 240-250 °C, WHSV within 1-2 g/g·h, at methanol/nitrobenzene molar ratio of (3-4):1 and hydrogen/nitrobenzene molar ratio (3-6):1. These reaction conditions and reagents ratios provide nitrobenzene conversion 99,5% and selectivity towards N-methylaniline 92 mol.%.

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Synthesis and metathesis polymerization of new fullerene-containing norbornens by catalyst Grubbs 1’st generation

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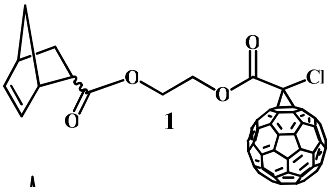
Fullerene containing thin polymer films are used as acceptor components of bulk heterojunction photovoltaic devices [1-3]. Although organic materials in solar cells are inferior to inorganic ones as far as turnaround efficiency of light (power conversion efficiency, PCE) is concerned, a number of their obvious advantages enables us to consider them as a possible alternative to traditional silicon batteries in future.

Due to low solubility of C_{60} it is difficult to obtain fullerene-based high molecular weight polymers. In this work we report the preparation and characterization of new fullerene-based monomers and a high molecular weight polymer containing C_{60}, obtained by via ring-opening metathesis polymerization and copolymerization (ROMP). The choice of the metathesis method is explained primarily by the irreversible polymerization of the norbornene monomers on the living catalyst system, the possibility of obtaining "block copolymers" and simplicity of the experiment and ease of its control [4].

The fullerene monomers **1-3** for ROMP was prepared by cycloaddition of malonic and dichloroacetic acid derivatives to C_{60}, purified by column chromatography, and characterized by ^{1}H, ^{13}C-NMR, IR, UF-spectrum, mass spectrometry (MALDI-TOF).



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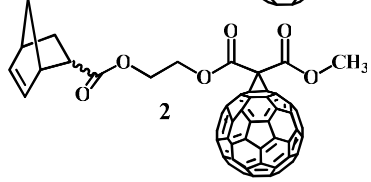

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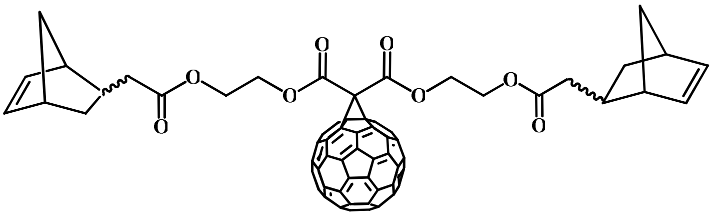

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Homopolymerization of monomers **1-3** was carried out under inert atmosphere at the presence of the Grubbs 1’st generation catalyst at room temperature in the CH_2Cl_2 solution. During the first 6 hours consumption of the initial monomers (TLC control) and precipitation were observed. The polymers is insoluble in $CHCl_3$, C_6H_6, $C_6H_5CH_3$, THF and EtOAc and is partially plumped at keeping in DMSO, so the molecular weight of polymers was impossible to estimate.

Thus, co-polymers of fullerene monomers **1-3** with related fullerene-free norbornenes in the ratio 1:1 have been decided to be synthesized for improving their solubility. Copolymerization proceeded quickly enough and the forming products were well dissolved in $CHCl_3$ enabling us to take its NMR spectra, determine its molecular weight and produce thin polymer films on its basis.

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Photocatalytic activity of TiO_2 thin films

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This paper considers the properties of thin-film photocatalysts based on titanium dioxide. TiO_2 thin films were deposited by means of ion-plasma installation «Yashma-5» with dual magnetron sputtering system (MS) in two configurations of magnetic field. The evaluation of photocatalytic activity was carried out on the decomposition of methylene blue. The more details are presented in [1]. The calculations of the bandgap are presented.

The thickness and structure of the film are determined its sorption, which greatly contributes to the efficiency of photocatalysis reaction. It was found that the increase of film thickness leads to significant increase in TiO_2 photocatalytic activity. The configuration of the magnetic field of the magnetron affect on films structure. Thus, it is a tool of change photocatalytic properties of thin films.

The dioxide titanium thin films with predominance of anatase structure were deposited by means of «closed» dual MS. For «mirror» configuration, values of bandgap are lower. It is evidence about mixed phase of TiO_2 films (anatase and rutile). The high photocatalytic activity is inherent to samples, which are deposited by «mirror» configuration.

The photocatalytic activity of experimental samples is higher than in the case of use RF magnetron [1]. Such magnetron configuration is considered as for deposition high quality thin films. The obtained results are similar to in the case of using thermal annealing [2].

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Silica-supported Mn-containing Ag catalysts for ethanol oxidative dehydrogenation

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Annual production of bioethanol in the world steadily grows and according to some predictions it may reach about 280 billions tons by 2020 year. Therefore bioethanol may be used as cheap and easy available raw for production of different organic compounds, in particular, acetaldehyde. Design of highly effective catalysts for ethanol dehydrogenation is important problem. High activity and selectivity of silver catalysts supported over Si_3N_4 and SBA-15 in oxidation of alcohols was shown in [1, 2]. Activity of supported silver catalyst may be increased by addition of transition metal oxides, such as Ce, Mn, Fe and Co. Catalytic properties of transition metal oxides is adjusted, mainly, by efficiency of redox cycle. According to [3] activation of molecular oxygen and catalytic activity of transition metal oxides depends on band gap energy. So, catalytic activity of oxide-semiconductors in CO oxidation decreases with increasing of band gap energy [3]. Band gap energy for CeO_2, Fe_2O_3, Co_3O_4 and MnO_2 oxides is equal to 3.0-3.2, 1.82-1.96, 1.6 and 1.3 eV respectively. Thus, manganese oxide is expected the best modifier for oxidative catalysts with this point of view. Indeed, high activity of Ag/MnO_x catalysts in selective oxidation of organic compounds, in particular, benzyl alcohol [4], octanol-1 [5] and ethanol [6] was shown.

The purpose of present research work is to study the effect of structure and nature of MnO_x oxides on the catalytic activity of $Ag/MnO_x/SiO_2$ catalysts in ethanol dehydrogenation (aerobic and anaerobic) and CO oxidation. According to TPR data the reducibility of MnO_x increases in presence of silver. The hydrogen consumption peaks for $Ag/MnO_x/SiO_2$ sample is shifted significantly to low temperatures in comparison with MnO_x/SiO_2 sample. However, degree of reduction of manganese oxides is similar for both samples. Similar effect observed for unsupported «noble metal / transition metal oxide» catalysts is widely discussed in literature and commonly associated with spillover of oxygen from oxide to Ag particles or spillover of hydrogen from Ag to the oxide surface. In the present work it is noticeable that increasing of reoxidation capability of MnO_x/SiO_2 samples in presence of silver was observed by means of TPO analysis. Reoxidation of MnO_x/SiO_2 and $Ag/MnO_x/SiO_2$ samples occurs in two steps at the same temperature regions, however, amount of consumed oxygen in TPO mode for MnO_x/SiO_2 sample is significantly smaller than for $Ag/MnO_x/SiO_2$. One of reasons of the reoxidation rate growth may be associated with the effect of silver additives on the lattice oxygen mobility in Mn-containing oxides and/or facilitate activation of molecular oxygen on the surface of MnO_x. On other hand, MnO_x may affect on the properties of Ag nanoparticles. Difference between catalytic activities of Ag/SiO_2 and $Ag/MnO_x/SiO_2$ samples was observed in dehydrogenation of ethanol. So, ethanol conversion was achieved up to 31 % and 13.7 % at 240 ^oC for $Ag/MnO_x/SiO_2$ and Ag/SiO_2 samples respectively. Activities of the samples are similar in oxidation of ethanol, however, increasing of CO_x yield at above 220 ^oC was observed for $Ag/MnO_x/SiO_2$ sample in comparison with Ag/SiO_2.

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Photo- and X-ray sorption, photocatalytic properties of magnesium fluoride

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Magnesium fluoride finds a wide application in optic and catalytic branches of industry. In this connection the investigation of MgF_2 surface properties as well as the search for new effective photosorbents and photocatalysts is of great importance now. This paper is aimed at investigating photo-, X-ray sorption and photocatalytic properties of magnesium fluoride.

The complex of experimental and theoretical methods of study allowed detecting photosorption of simple molecules (O_2, H_2, CH_4, CO, CO_2), and also X-ray sorption of oxygen on the surface of magnesium fluoride, and photosorption of oxygen connected with colour centres which were induced by X-ray radiation. The adsorption centres generated or activated by illumination of a sample with the full light of a mercury lamp reveal both electron-acceptor and electron-donor properties. Photosorption of acceptor molecules (O_2, CO_2) was detected to be realized more actively. The identity of oxygen and carbon dioxide photosorption centres was shown. The following moments were distinguished as the peculiarities of photo- and X-ray stimulated processes: non-reversibility and saturating capacity, the presence of photo stimulated post sorption, and the influence of the sample prehistory. On the basis of photo- and X-ray sorption properties of magnesium fluoride investigation three spectral areas were found out which corresponded to fundamental absorption and absorption of induced colour centres. The differences in activity of passing the processes stimulated by radiation, in kinetics and thermo-desorption spectra of the oxygen being sorbed, is observed depending on the excitatory region.

As a result of photocatalytic properties on the surface of magnesium fluoride experimental study the reactions of dark oxidation of hydrogen, photo oxidation of H_2 and CO, and photolysis of CO_2 were found out. A probable mechanism of hydrogen photo oxidation reaction was suggested on the basis of fulfilled kinetics investigation. The necessary stage of the process is considered to be the photosorption of oxygen. In the limiting stage of the reaction electron-excited forms of photosorbed oxygen interact with molecular hydrogen of a gaseous phase and they are deactivated with the oxygen of a gaseous phase.

In the paper the kinetics of carbon oxide (II) interaction with pre-photosorbed oxygen and with that of a gaseous phase on the surface of MgF_2 under the action of UV radiation was thoroughly studied. The suggested mechanisms are notable for possible ways of deactivation of the active oxygen forms. The low temperature form of oxygen is an active one in photo oxidation of CO. The photo desorption of oxygen is a process which competes with the photosorbed oxygen photo stimulated with the reaction of CO oxidation. When the reaction occurs from the gaseous phase the active forms of photosorbed oxygen are deactivated by the oxygen of a gaseous phase.

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Toluene ethylation with ethanol on zinc-promoted h-pentasil zeoliten

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The toluene ethylation products *p*-and *m*-ethyltoluenes are used for the manufacture of methylstyrene and polymethylstyrene, thus opening new frontiers for the utilization of toluene and allowing it to replace benzene, which is in shorter supply, in petrochemical synthesis[1,2]. Conventional acid catalysts of the $AlCl_3 \cdot HCl$ type used for alkylation have significant drawbacks (corrosion of equipment, a high catalyst consumption, environmental pollution, etc.). A new promising process for the manufacture of *p*-ethyltoluene is the ethylation of toluene over high-silica (HS) zeolites of the ZSM-5 type. The promotion of H-pentasil zeolites with various elements (B, P, Mg, Si, etc.) results in the enhancement of their *para*-selectivity[3,5]. A great interest in this context is the development of these so-called *para*-selective catalysts for toluene ethylation. The objective of this work was to study the influence of the physicochemical and catalytic properties of the modification of an H-pentasil zeolite with zincon in the toluene ethylation reaction. The catalysts promoted with 2.5– 10.0 wt % zinc were prepared by the impregnation of the H-form with a zinc acetate solution at 80°C over 6 h. The samples were dried in air for 16 h and then for 4 h in a drying oven at a temperature of 110°C and were calcined for 4 h in a muffle furnace at 500^oC. The temperature of the reaction had no effect on the conversion of alcohol, which was 92–100%, whereas the toluene conversion increased from 24.5 to 39.3 wt % with the temperature. Along with toluene and ethyltoluene, C_{5+} aliphatic hydrocarbons, benzene, ethylbenzene, xylenes, trace trimethylbenzenes, and other aromatic hydrocarbons were detected in the hydrocarbons portion of the catalyzate. The introduction of zinc via the impregnation of zeolite with a zinc acetate solution followed by the decomposition of the salt at 550^oCleads to a substantial change in the catalytic and physicochemical properties of the catalyst; their activity in the alkylation and disproportionation reactions of toluene is reduced and the selectivity for *p*-ethyltoluene increases.The introduction of zinc in an amount of 2.0–10.0 wt % to ultrasil enhanced its *p*-ethyltoluene selectivity from 42.3 to 70.1%. The physicochemical and catalytic properties of zincpromoted H-pentasil were examined in the toluene ethylation reaction. It was shown that the gradual weakening of the acid properties of with an increase in the Zn loading of the zeolite is explained in terms of the fact that a portion of H^+ ions is exchanged for Zn^{2+} ions (or Zn(OH)+ ions produced by hydrolysis of zinc acetate) during the impregnation of H-pentasil with the zinc salt and the base oxide ZnO, which can react with H^+-zeolite according to the scheme $ZnO + 6H^+ \rightarrow Zn^{2+} + H_2O$, is produced after the decomposition of the salt. A portion of zinc remains in the channels and on the external surface of the zeolite crystals, changing the size of both the channels and the channel windows. As a result, the protic acidity of the catalysts and their activity in the alkylation reaction decrease and the diffusion characteristics of the zeolites, which are responsible to a great extent for the *para*-selectivity of catalytic systems, change as well.

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Study of Pd and Pt catalysts supported by zirconia and ceria-zirconia oxides for 5-nonanone hydrogenation

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Currently the development of supplementary methods for obtaining motor fuels and valuable chemicals by biomass processing is a promising way for sustainable development of global chemical industry. Organic acids, the largest group of the promising biomass derivatives, can be produced by fermentation and/or chemical transformation of glucose obtained by biomass hydrolysis. Carboxylic acids can be converted into ketones accompanied by carbon dioxide and water release via catalytic decarboxylation of two acid molecules in the presence of metal oxides. Earlier, we shown that ZrO_2 and CeO_2/ZrO_2 are the most effective catalysts of valeric acid ketonization into 5-nonanone [1]. One-pot process of carboxylic acid decarboxylation followed by ketone hydrogenation into alkane over Pt(Pd)/M_xO_y bifunctional catalyst can be considered as a more attractive way to produce green diesel components probably providing higher selectivity due to immediate hydrogenation of adsorbed intermediate products of ketonization.

The goal of the present work is to find catalyst(s) with optimal properties for one-pot process of valeric acid decarboxylation followed by 5-nonanone hydrogenation into n-nonane. Pd and Pt catalysts supported by ZrO_2 and CeO_2/ZrO_2 for 5-nonanone hydrogenation were characterized by XPS, HRTEM, BET, size effect of Pd particles and influence of by-products on catalytic activity in the process were studied. The hydrogenation was carried out in a fixed bed flow reactor in the gas phase at 543-628 K under hydrogen at ~6-10 bar.

Based on the results obtained, complex of acid-base properties and specific surface area could be responsible for activity of Pd and Pt catalysts in ketone hydrogenation. The negative effect of by-products of valeric acid ketonization (CO_2 and H_2O) and 5-nonanone hydrogenation (5-nonanol) on catalytic activity of platinum and palladium supported by zirconia and ceria-zirconia was found. No metal size effect was observed for Pd/ZrO_2 catalyst. Also the stability of all catalysts was studied. The most active and stable catalysts were found for one-pot conversion of valeric acid to 5-nonanone.

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Carbon dioxide conversion of methane for engine and power units

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A hypersonic aircraft has been actively developing in recent decades, it would solve the problem of the active energy interaction with the air flowing around it. The principle of organization energy systems of such devices is in the use of the kinetic energy of air flow, which is converted by separate board systems to other types of useful energy.

Another way of energy exchange – is a system of active thermal protection [1]. The basis of this system is the utilization of heat of aerodynamic heating and power unit in the most heat-stressed parts of the construction of hypersonic aircraft. This heat can be used for various physical and chemical processes, such as heating of energy carriers and conducting of endothermic catalytic reactions involving hydrocarbons. Thus, this system not only provides a normal temperature setting of the aircraft, but also the production of synthesis gas containing molecular hydrogen, which is used as fuel.

Carbon dioxide conversion of methane is one of these endothermic reactions, it is described by the following equation:

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 - 248\ \text{kJ} \qquad (1)$$

Supported nickel catalysts are the most prefered for this reaction. The noble metals (Ru, Rh, Pt) can also be used as an active component, but they are relatively expensive and less available.

It would not be effective to use the pelletized catalyst for carrying out the endothermic catalytic reactions in the systems of heat utilization of hypersonic aircraft, as in the conditions of the mobility of the reaction space itself a tendency of pellets to migration and repacking will be enhanced, it will lead to their intensive attrition and shattering. Also the catalysts for such systems have to satisfy a number of specific properties, namely: to be a part of the heat-exchange surface, to have a high thermal conductivity, a low hydrodynamic resistance of the catalytic elements, a high adhesive resistance of material. The catalytic coating (planar catalysts), deposited directly on the heated wall, satisfies these requirements.

Such coatings can be obtained by gas-dynamic spraying of catalytically active composition of the nickel-aluminum system on the heat-resistant surface, by plasma coating a porous layer of the secondary carrier, by coating the activator by magnetron or chemical method.

The main obstacle to the application of this process is the rapid-growing deactivation of catalysts due to their coking and sintering of active metal particles.

There are two ways of coke formation:

dissociation of methane:

$$CH_4 = C + 2\ H_2 - 74{,}8\ \text{kJ} \qquad (2)$$

disproportionation of carbon monoxide (Boudouard reaction):

$$2\ CO \leftrightarrow C + CO_2 + 172{,}5\ \text{kJ} \qquad (3)$$

Soot formation can be reduced by introduction of excess of carbon dioxide, by diluting the mixture by neutral or circulation gas, or steam, which produced during reverse water-gas shift reaction, which may occur along with reaction (1).

The catalysts supported by basic carriers are least influenced by coke formation. Thus, Ni/Al_2O_3 has the highest activity in the prime period of operation, but Ni/MgO, Ni/CaO, Ni/ZrO_2, Ni/MnO surpass this one in operational functionality and in resistance to coke formation.

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Catalytic combustion of methane on metal-containing zeolite catalysts

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In recent years development of the catalytic combustion technology of natural gas and other hydrocarbon fuels is actual, for example, for the development of environmentally friendly catalytic gas turbines. Methane is currently the second most important greenhouse gas emitted from human activities (carbon dioxide is first one). But on a per molecule basis, methane is a much more effective greenhouse gas than CO_2. The potential contribution of methane to the global greenhouse effect has proven to be about 20 times stronger than carbon dioxide. Thus, the complete combustion of methane to carbon dioxide is very actual and important task. One of the major problems is the search for suitable catalysts having high activity and thermal stability [1-4].

The aim of this work is the synthesis of effective metal-containing zeolite catalysts for the gas-phase oxidation of methane, development a method of formation and stabilization of active states of metals on the surface of ZSM-5.

The following systems were investigated for the process of complete oxidation of methane: 7Ag/ZSM-5, 7CuO/ZSM-5, $7Co_3O_4$/ZSM-5, $7Fe_2O_3$/ZSM-5, $7CeO_2$/ZSM-5 и 7NiO/ZSM-5. For the preparation of catalysts we selected three main methods: the deposition-precipitation method, ion exchange method and incipient wetness impregnation method. The best results have been obtained using the method of incipient wetness impregnation, besides this method is waste less unlike deposition-precipitation and ion exchange methods. Before carrying out oxidation process the catalysts were pretreated in: inert, reducing, oxidizing and oxidation-reduction atmospheres. Activity catalysts for oxidation reaction of methane was studied in a reaction gas mixture (5 % CH_4 + 11 % O_2 + 86 % Ar) in a flow reactor.

It was found that after the reduction pretreatment the activity of catalysts increases significantly. According to activity in the process complete oxidation of methane investigated catalysts can be arranged in the following series: 7CuO/ZSM-5 > $7Co_3O_4$/ZSM-5 > 7Ag/ZSM-5 >$7Fe_2O_3$/ZSM-5 > $7CeO_2$/ZSM-5 > 7NiO/ZSM-5 (after reduction pretreatment). The 7 Cu/ZSM-5 sample after pretreatment in a reducing atmosphere has most active in this process, complete conversion of the methane was observed at 500 ° C, but at 400 ° C, the methane conversion was 99.48% and at 450 °C - 99,85%.

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Alkylation of ethylbenzene with a saturated monatomic c_4 alcohols over modified zeolite cataysts with ree

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Demand for isomers of alkyl aromatics to dialkylated compounds via simple alkylation, trans alkylation, or disproportionation is commercially importants intermediates in the synthesis of dyes pigments, photographic materials and films are currently increased. For example, p-alkylated ethylbenzenes are used to produce p-alkylated styrenes, the monomers for poly (p- alkylated styrenes), which have high glass-transition temperatures (Tg) compared with polystyrene [1]. One of the main methods of obtaining dimethyl-ethyltretbutyl and dimetyl-butylbenzene is catalytic alkylation of ethylbenzene with tretbuthyl alcohol on acid catalysts.

In a recent years, particular interest as catalysts for alkylation of alkylaromatic hydrocarbons with alcohols are synthetic zeolites modified by multiply charged cations. In many alkylation processes, the meta-isomer, rather than the ortho- and para-isomers, is formed, but para-selective alkylation has been attempted in most alkylations. para - Selective alkylation was first demonstrated by Mobil researchers for the production of p-xylene [2, 3].

The aim of this work is study the catalytic properties of anionic and cationic forms of zeolities Y-type (partly loaded with rare earths) in alkylation reaction of ethylbenzene with tretbuthyl alcohol.

Catalysts were synthesized from Y-type zeolite having molar ratio with SiO_2/AlO_3 is equal to 5. Ca- and REECaY type of zeolites were obtained by ion exchange method. The catalyst was activated at 500^0C for 2 h in a controlled stream of air. Tret-butylation of ethylbenzene with tret-butyl alcohol as the alkylating agent was carried out on a fixed vertical down-flow reactor. 4 cm^3 volume of catalys was placed in a reactor and heated at atmospheric preassure in a controlled hydrogen in the temperature range of $150\text{-}200^0$C. The optimum feed ratio (ethylbenzene : t-butyl alcohol) was 2:1 and feed rate was 1,0 h^{-1}. The reactants were fed into the reactor using a syringer infusion pump. The products collected in the receiver flask were analyzed in a Agilent 7890-A gas chromatograph equipped with a capillary column and a flame ionization detector.

It was established that the convertion of aromatic hydrocarbons, alcohols and the selectivity of 1-ethyl-4-tret-butyl-benzene (ETBB) and 1,2 dimetylbutyl benzene (DMBB) depend on the degree of ion exchange and the nature of multiply charged cations. Over HoCaNaY at a 160^0C temperature deliveration of DMBB and ETBB consist of 75-78% from the theoretical point and a selectivation is 75-78%.

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A New Type of Polymeric Catalysts for Cellulose Conversion to Hexitols

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Cellulose is one of the mostly wide-spread organic materials on the earth. It has been estimated that 10^{11}–10^{12} tons of cellulose are synthesized in nature annually. It is mostly combined with hemicelluloses and lignin in the plant cell walls [1]. Cellulose is considered a likely alternative to fossil fuels as its renewable resources can provide the production of raw materials for the chemical industry and second-generation biofuels on a large scale [2, 3]. Moreover, at present, taking into consideration constantly increasing expenses on hydrocarbon fossil fuel mining, chemicals obtained from cellulose biomass can be much cheaper than those obtained from oil [4].

A large number of hydroxyl groups in cellulose allow for its conversion to polyols [5]. First, cellulose is hydrolyzed to glucose which is then hydrogenated under hydrogen pressure > 2 MPa in the presence of a catalyst to form sorbitol (for the most part), mannitol and some amount of C_2 – C_5 polyols.

In this paper a new type of Ru-containing catalysts based on non-functionalized and functionalized hypercrosslinked polystyrene (HPS) is proposed for cellulose hydrolytic hydrogenation. HPS is characterized by ultra-high porosity and excellent sorption properties and was successfully used as a support for nanocomposite catalysts.

Cellulose conversion to polyols was carried out in a subcritical water under the following conditions: temperature 245 °C, hydrogen partial pressure 6 MPa, propeller stirrer speed 600 rpm. The experiments were performed in a steel reactor (50 cm^3, Parr Instrument, USA). Microcrystalline cellulose (0.5 g), a catalyst (0.07 g) and 30 mL of distilled water were loaded into the reactor. At the end of the experiment the catalyst and non-hydrolyzed cellulose were separated by filtration. The weight of the non-hydrolyzed cellulose was determined as the difference between the weight of the residue on the filter and the catalyst weight. The content of the conversion main products was determined by chromatographic methods in liquid and gas phases. For the analysis of a gas phase, gas chromatograph Crystallux-4000M (MetaKhrom, Russia) was used, while for the liquid phase, highly effective liquid chromatograph UltiMate 3000 (Dionex, USA) was employed.

Ru-containing catalysts based on HPS were studied in hydrolytic hydrogenation of cellulose. We demonstrated that only the catalysts based on non-functionalized MN-270 provide high efficiency and selectivity towards hexitols due to stability of the HPS framework resulting in high surface areas of the catalysts and well-defined Ru nanoparticles. The catalysts based on functional analogues of MN-270, i.e., MN-100 and MN-500, were practically inactive in this process.

The use of the 1.0% Ru/MN-270 catalyst allows achieving the total sorbitol and mannitol yield about 50% at the ~85% conversion that is comparable with the results obtained with more complex and expensive catalytic systems. Moreover, preliminary studies show that the temperature decrease and the increase of the process duration result in the increase of the hexitol yield up to 60 – 70 %. This catalyst is also highly stable in the repeated use making it promising for cellulosic biomass conversion to feedstock for chemical synthesis and industrial production of second-generation biofuel.

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Effect of coke formation on ZSM-5 catalysts for conversion of synthesis gas to dimethyl ether

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Dimethyl ether (DME) is an important chemical raw material for many chemical compounds, such as dimethyl sulfate, methyl acetate and light olefins. DME is also used as a propellant for aerosol containers since it is environmentally safe [1].

The most common catalysts in the literature for the process of producing dimethyl ether from synthesis gas are physical mixtures of methanol synthesis catalysts and zeolites ZSM-5 type. Due to the particular structure of zeolites have the property of a molecular sieve selectivity, zeolites are capable of absorbing only a substances of a certain size molecules. Also zeolites are classified as superacids, because of their unusual acidic properties. Therefore zeolites essential for use in many petrochemical processes, where they show higher catalytic activity than that currently used in traditional catalyst systems. During the reaction, ZSM-5 catalyst is deactivated by the buildup of carbonaceous residues (generally termed coke) which block access of reactant molecules to the active sites [2]. The study of carbonaceous residues on the surface of ZSM-5 zeolite in the synthesis of DME, is an urgent task, the solution of which is the key to choosing the optimal dehydration catalyst.

The purpose of this article is an investigation of the effect of coke on the physicochemical and catalytic properties of zeolite catalysts.

To study the deactivation during the synthesis of DME were selected two samples of zeolite: HZSM-5 (30) synthesized in the IPC SB RAS (sample 1) and HZSM-5 (30) of the company «Zeolyst International» (sample 2). Catalytic experiments were carried out in flow reactor at 3 MPa and temperature interval 200-260 °C. The bulk volume of catalyst was 5 cm^3, the rate of feed stream of $CO+H_2$ = 48 ml/min, the molar ratio of source gases $CO:H_2$ = 1:2. As a catalyst for methanol synthesis it was used $CuO/ZnO/Al_2O_3$ sample and as catalyst for hydration of methanol was used zeolite. Before starting work the catalyst was treated at a pressure of 3 MPa in a flow of hydrogen and a temperature of 300 °C for 3 - 5 h. Chromatographic analysis of the products was carried out on a gas chromatograph «Crystall 5000.2». Thermal analysis of samples performed by co-TGA-DSC Q-600 analyzer (TA Instruments, USA). The method of temperature-programmed oxidation (TPO) have been studied the possibility of oxidation of coke on the surface of the materials studied, the temperature range 25-900 ° C oxidation. Studies were carried out on samples obtained chemisorption analyzer «ChemiSorb 2750» (Micromeritics, USA). Defining the parameters of the porous structure and specific surface of the samples were determined by BET using automatic analyzer TriStar II (3020), produced by Micromeritics (USA).

In this paper have been studied the catalytic properties of zeolites, found that the catalyst activity is unchanged for 100 hours, after which there is a slight decrease in DME yield possibly due to the formation of products of condensation on the catalyst surface. The results of thermal analysis and temperature-programmed oxidation after 120 hours catalysis showed that on the sample 1 is formed by one form condensation products, and on the sample 2, one form. Quantity condensation products on the sample 1 are less than on the sample 2. Specific surface area and pore size for both samples after catalysis decreases. This is due to the formation of condensation products and partial filling of the pores. Nature of the change in pore size is the same for both catalysts.

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Transformation of n-hexane and stable section of hydrogenated feed on the surface of high-zeolite systems

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The present stage of social development is characterized by the steady growth of oil processing product consumption, increasing requirements to their operational and environmental characteristics. In this connection, the establishment of basic regularities and ways of controlled activation of the C–H bonds in hydrocarbon molecules is a priority lead in the domestic chemical science. ZSM-5-type zeolites find broad application as catalysts of various petrochemical processes and their examination is a perspective direction of oil processing.

With the purpose to study the catalytic activity of 1 % Ga-ZSM-5 in the H-form with a silicate module M = 100 mol/mol, studies were made on a laboratory plant of the flowing type within a temperature range of 250–500 ºC with a 50 ºC step, under atmospheric pressure, with no circulation of a hydrogenous gas, with a volume *n*-hexane feed rate of 1 and 2 h^{-1}.

Chromatographic analysis of the products was carried out on a *Crystal 5000* analytical stationary laboratory chromatograph designed for analysis of organic compounds with boiling temperatures up to 250 °C by gas-liquid and gas adsorption chromatography. The chromatograph was equipped with a DB-1 column 100 m long, of a 0.25 mm diameter, polymethyl siloxane being the stationary liquid phase. Helium served as the gas carrier. Component composition was analyzed by means of a flame ionization detector (FID). Components were identified with the use of the “*Alkylates*”, “*Naphtha*”, and “*Reformat*” standards. Activation of the catalyst under various conditions lead to a redistribution of the active redox centers on its surface, which in turn leads to a redistribution of reactions areas. In all cases, the conversion of n-hexane occur in three main directions: cracking, isomerization and aromatization. However, we can distinguish the following regularities:

1. In all cases, that we are considered temperature increasing increases the process conversion. Conversion of n-hexane with increasing volumetric flow rate of the raw material (decrease the contact time raw material with the catalyst) is reduced. Depth conversion under similar conditions above on the catalyst, which was activated in a current of air.

2. Cracking reactions selectivity increases with increasing temperature. Selectivity of the cracking reactions for catalyst activated in a stream of air with increasing feed rate decreases. The catalyst is activated in a stream of hydrogen virtually unchanged or slightly increased. Selectivity for cracking reactions under similar conditions lower than the catalyst activated in a stream of hydrogen.

3. Isomerization reaction selectivity is decreased with increasing temperature. With increasing volumetric feed rate selectivity of isomerization reactions is increased in all cases. Selectivity of isomerization reactions under the same conditions had significantly higher, than for catalyst is activated in a current of hydrogen.

4. Aromatization reactions selectivity increases with increasing temperature in all cases. Aromatization reactions selectivity of a catalyst is activated in air, with increasing feed rate - is reduced to 400 °C and increases slightly or does not change with increase temperature. The catalyst is activated in a current of hydrogen is reduced significantly by increasing the feed rate. At lower feed rates, the aromatization reactions selectivity higher at a catalyst activated in a current of hydrogen. By increasing the feed speed - reverse.

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Temperature hysteresis of bimevox-perovskites in isobutanol dedydrogenation reaction

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Solid electrolytes (SELs) with lamellar framework structure are of considerable interest for catalytic chemistry since the scope of these materials can be expanded by varying their composition by replacement of cations in the base compound with reactive dopant ions. Complex oxide materials belong to the SEL class with anionic (oxygen-ionic) conductivity type and have perovskite-like structures. These oxides are based on the bismuth vanadate $Bi_4V_2O_{11-\delta}$ [1]. Bismuth vanadate and its derivatives exist in several polymorphic modifications (α, or monoclinic; β, or orthorhombic; and γ, or tetragonal).

The samples of $Bi_4(V_{1-x}Me_x)_2O_{11-\delta}$ with Me – Cu^{2+}, Fe^{3+}, Zr^{4+} (BIMEVOX) were obtained by the solid state synthesis, and were characterized by XRD, IR, XPS [2]. Catalytic activity of BIMEVOX was tested under flow conditions with chromatographic analysis of the reaction products in the cycle «heating (↑) – cooling (↓)» for checking the existence of a temperature hysteresis (TH) for BIMEVOX-catalysts. The changes of the yield of aldehyde – the main product of isobutanol conversion in stationary conditions $\Delta N = \frac{N\downarrow - N\uparrow}{N\uparrow} \times 100\%$ are shown below. In all case the TH is revealed in form «clockwise» and it decreases with xM increasing, so the influence M content and structural type of catalyst on TM is clear.

The effect of TM can be associated with the change of Arrhenius plots characteristics – the apparent activation energy of reaction $\boldsymbol{E_a}$ and pre-exponential factor $\boldsymbol{N_0}$ which connects with the number of the surface active centers. These values depend on charge of ion-dopant M as well as M content with the most active BIMEVOX in γ-phase [3-5]. As it can be seen from the table the TH connects with an increase of the activation energy ($\boldsymbol{E_a}\downarrow/\boldsymbol{E_a}\uparrow$) for the dehydrogenation cooling system in case of γ-BICUVOX and α,β- BIFEVOX catalysts. In case of BIZRVOX decrease values $\Delta \boldsymbol{N}_{350°C}$ (–60, –24, +5) is due to lowering the pre-exponential factor $\ln(\boldsymbol{N_0}\downarrow/\boldsymbol{N_0}\uparrow)$ (–2.0; –6.6; –16.6), that characterizes the deactivation of active centers.

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Partial n-hexane oxidation on Co and Mn-substituted aluminophosphates

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Partial oxidation is one of the most promising ways of transformation of cheap and available alkanes to more valuable products. n-Hexane oxidation is the model reaction of oxidation of light alkane to acids, which can be used in enhanced oil recovery. Among the catalyst of alkane oxidation different compounds based on transition metals, such as Co, Mn, Fe, Cu, are widely used, because of their possibility to change the oxidation state with initiation of radical chain mechanism of alkane oxidation. The promising catalysts for alkane oxidation are metal-substituted aluminophosphates, which combine advantages of heterogeneous systems with high catalytic reactivity of transition metal cations, because possibility of metal ions in framework position to change the oxidation state [1].

In present work the Co and Mn substituted aluminophosphates were used as heterogeneous catalyst in n-hexane oxidation by air. The reaction was carried out in a stainless steel batch reactor equipped with a magnetic stirrer under continuous flow of air during 24 hours. The system was pressurized with air and then heated under permanent stirring. The operating temperature was 150 ºC, the operating pressure after heating was maintained at 35 atm.

The non-catalytic and catalytic oxidation with Co and Mn-AlPO-5 were carried out and it was shown that the n-hexane conversion were higher in the case of using CoAlPo-5 and the main product distribution differed for non-catalytic and catalytic reactions. In the experiment without catalyst deeper oxidation was observed, compared with experiments with both Co and Mn-AlPO-5.

According literature data the metal substituted aluminophosphates are stable in oxidation of alkanes up to the 10 % alkanes conversion because of acids formation with leaching of active metal sites [2]. In this work the conversion of n-hexane was reached 26,9% with 93,9% selectivity to acids for Co-AlPO-5 without any leaching. The stability of catalyst to leaching was proved by XRF, the metal content in fresh and spent catalyst were 1,5%. The XPS was used to determine the oxidation state of Co in fresh and spent catalysts. It was shown, that in the spent catalyst the part of Co was in oxidation state 2+, while in the fresh catalyst cobalt was in oxidation state 3+. The h-hexane conversion on the spent Co-AlPO-5 was similar as on the fresh one, but the distribution of the main products differed. With re-used **CoL** the alcohols and ketones formed in smaler amount and the selectivity to acids increased in the same manner as in non-catalytic oxidation. This is due to partial transformation of Co^{3+} in the fresh catalyst to Co^{2+} in spent one which leads to changes in the product regulation function of catalysts.

The unexpected result was obtained with increasing the catalyst content in system. In the experiment with 100mg of catalyst instead of 20 mg in usual experiment the conversion of n-hexane decrease dramatically from 15,1 to 4,8 mol.%. The observed result can be explained by inhibitive property of catalyst, which appears in formation of significant amount of active intermediates on the catalyst surface without further oxidation of these intermediates by air with formation of reaction products.

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Physical-chemical characteristics and activity of hy-zeolite catalyst based on aluminium pillared montmorillonite for cracking of vacuum gasoil

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It is known that one of the conditions for a successful application of cracking catalysts is their stability. Increase the stability of contacts can be achieved by using bentonite clays as the matrix and binder. In the initial state, the natural materials are less suitable as supports for refining catalysts due to a low specific surface, pore volume and a high content of alkali cations. Modification of natural montmorillonite (NaMM) by pillarization allow to optimize its properties while maintaining high stability.

The aim of this work was to study the physico-chemical, acid and strength characteristics of HY - zeolite catalysts based on aluminum-pillared montmorillonite in the Na-form and their activity in the cracking of vacuum gasoil (VG) with the end of boiling point 570^0 C.

H-form zeolite NaY was prepared by ion exchange in a triple 1N NH_4 Cl. For pillarization NaMM used aluminum hydroxocomplexe $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^7$. Composite contained zeolite and pillared MM was formed into catalysts granules. Textural characteristics determined by the adsorption and desorption isotherms of nitrogen on the device "Accusorb" (BET method), acid characteristics - temperature programmed ammonia desorption method. Control of the phase composition was performed by X-ray on the device "DRON-4 * 0.7" with CuKα - radiation. Elemental analysis of the composites was carried out using energy dispersive X-Ray fluorescence spectroscopy on energy dispersive microanalysis system INCA - Energy 450 mounted on a scanning electron microscope JSM6610LV, JOEL, Japan. It is shown that the content of sodium decreases from 1.3 to 0.28% after the pillaring.

According to the data obtained on a universal testing machine Autograph AG- 100 GOST 8817-82 kNX «jumping-up test method» granules of synthesized catalysts differed high strength and withstand loads up to 306 kg/sm^2.

It is shown that pillarization increases the specific surface area of 48.2 m^2 /g NaMM to 379.9m^2 /g Al (7.5) NaMM. For HY - zeolite catalysts S increases in the sequence 149,3; 180.7; 211.6 m^2 /g for Al (2.5) NaMM, Al (5.0) NaMM, Al (7.5) NaMM, respectively. X-ray diffraction data confirmed that the crystal structure at NaMM pillarization saved. The first basal reflection (d_{001}) for Al (7.5) NaMM + HY increases compared with NaMM at 6,75 Å. The total number of averages (T_{des} = 200-300^{0}C) and strong acid sites (T_{des} > 300^{0}C) with a total acidity of 246 micromoles NH_3 / g NaMM maximal (57%) of the HY-zeolite catalyst Al (7.5) NaMM. It is shown that the greatest amount of light products (45.4%) and light diesel oil in their composition (37.1%) formed on HY / Al (5.0) NaMM - the catalyst, and the greatest amount of gasoline (14.6%) - on HY / Al (7,5) NaMM. Gasoline formed at VG cracking on Al (7.5) NaMM + HY catalyst distinguishes the smallest content of aromatic hydrocarbons (17.9%) and olefins. Increasing the concentration of Al in the matrix pillared catalyst leads, moreover, to increase isomerization activity. Isomer content in gasoline produced by cracking on Al (7.5) NaMM + HY-catalyst reaches 32.4%. The presence of large amounts of iso components in gasoline makes it attractive as a component of commercial gasoline. It should also be noted that the cetane number of light gasoil according to the analysis on the Octane Meter SX -100 M, equal to 63. In the gas phase (17.6%) showed the formation of 8.7% methane, 5.4% ethane, 7.2% ethylene, 21.3% propane, 15% propene, 35.4% butane and 9.8% isobutane.

From analysis of the above data it can be concluded that HY composites on the base pillared AlNaMM, characterized by high strength, can be used to obtain light products from weighted vacuum gasoils.

Photocatalytic activity of TiO_2 thin films

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This paper considers the properties of thin-film photocatalysts based on titanium dioxide. TiO_2 thin films were deposited by means of ion-plasma installation «Yashma-5» with dual magnetron sputtering system (MS) in two configurations of magnetic field. The evaluation of photocatalytic activity was carried out on the decomposition of methylene blue. The more details are presented in [1]. The calculations of the bandgap are presented.

The thickness and structure of the film are determined its sorption, which greatly contributes to the efficiency of photocatalysis reaction. It was found that the increase of film thickness leads to significant increase in TiO_2 photocatalytic activity. The configuration of the magnetic field of the magnetron affect on films structure. Thus, it is a tool of change photocatalytic properties of thin films.

The dioxide titanium thin films with predominance of anatase structure were deposited by means of «closed» dual MS. For «mirror» configuration, values of bandgap are lower. It is evidence about mixed phase of TiO_2 films (anatase and rutile). The high photocatalytic activity is inherent to samples, which are deposited by «mirror» configuration.

The photocatalytic activity of experimental samples is higher than in the case of use RF magnetron [1]. Such magnetron configuration is considered as for deposition high quality thin films. The obtained results are similar to in the case of using thermal annealing [2].

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One step catalytic synthesis of cumene from benzene and acetone

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Nowadays cumene is obtained by catalytic alkylation of benzene with propylene. The most part of cumene is used as precursor for phenol, which is synthesized by decomposition of cumene hydroperoxide. The main and unavoidable disadvantage of cumene method of producing phenol is acetone formation, which is a low value by-product of the process. While the phenol used in the synthesis of plastics (bisphenol A), pharmaceuticals, resins, acetone production exceeds its consumption. That's why it is of great interest to recycle acetone and to produce cumene by one step catalytic synthesis from acetone and benzene.

A series of bifunctional catalysts involving hydrogenating and alkylatiing components has been prepared. Hydrogenating component of the catalysts involved 11 wt.% Cu supported on silica. Alkylating components involved zeolites MOR, BEA, FAU or MFI with similar Si/Al ration (10-12.5). The materials were characterized by elemental analysis, TPR H_2, TPD NH_3, TEM, nitrogen adsorption-desorption. The catalysts were tested in hydroalkylation of benzene with acetone. The catalytic experiments were carried out in a fixed bed reactor at 130-210 °C under 0,1-3 MPa, the acetone/benzene/hydrogen molar ratio was (1:4-9):1.2, the weight hourly space velocity (WHSV) of benzene/acetone mixture was 3 h-1.

Study of benzene interaction with acetone in the presence of hydrogen over bifunctional catalyst showed that reaction pathways and stability of catalyst depends on the relative position of the hydrogenation and alkylating components. The best result was obtained over the catalytic system organized in layers, involving first hydrogenating catalyst and then alkylation catalyst.

Variation of the type of the alkylating component suggested that the highest catalytic activity can be achieved over large pore zeolites, such as MOR or BEA, while the highest selectivity to the products of alkylation was reached over zeolite BEA.

It has been demonstrated that acetone conversion increased by in factor of 3 when the reaction pressure was raised from 0,1 to 1 MPa, on the contrary selectivity to cumene depends primarily on reaction temperature and benzene/acetone molar ratio. The increase of reaction temperature from 130 °C to 170 °C results in the increase of the contribution of alkylation products, but further increase of reaction temperature to 230 °C leads to the selectivity drop down due the higher contribution of the products of acetone condensation.

The best catalyst performance has been achieved over Cu/SiO_2-BEA catalyst at 170 °C, 1 MPa, the benzene/acetone molar ratio of 9. Over this catalyst the conversion of acetone reached 98%, while selectivity to the products of alkylation was 94%.

Thus, the alternative route of cumene synthesis by hydroalkylation of benzene with acetone has been demonstrated over bifunctional catalyst involving copper-containing component and zeolite beta. The conversion of acetone and selectivity to cumene achieved over this catalyst reached 98% and 84%, respectively.

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The role of active sites in destructive sorption of CF_2Cl_2 over nanocrystalline MgO and VOx/MgO

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Halocarbons, especially the ones containing no hydrogen atoms, are extremely stable and are believed to destroy the Earth ozone layer. Therefore, development of active destructive sorbents capable of their decomposition without harming the environment is of substantial practical interest. Small amounts of vanadium added to nanocrystalline MgO aerogels were shown to promote their activity in destructive sorption of halocarbons. This reaction is characterized by prolonged induction period, which is considerably shortened after the addition of the studied promoter.

In the reaction with CF_2Cl_2, the samples of nanocrystalline MgO aerogels with vanadium concentrations 0, 1, 5, 10 wt. % were studied. The sample was loaded into an ampoule used for EPR measurements and activated in 30 ml/min nitrogen flow for 1 hour. Then the reaction with CF_2Cl_2 was carried out with the following spin probe adsorption. The perylene solution in toluene (2×10^{-2} M) was used as the probe. The concentration of active sites was measured by EPR method immediately after adsorption and after heating for 18 hours at 80°C.

It was found that addition of vanadium had a catalytic effect on the interaction of nanocrystalline MgO aerogels with halocarbons, accelerating the formation of the active sites on the surface of the nanoparticles. A good correlation between the rate of destructive sorption reaction and the concentration of electron-acceptor sites was observed.

The electron-acceptor sites on the surface of initial samples of MgO and VOx/MgO were not found. Their concentration gradually increased during the induction period, reaching a clearly defined maximum in the active state when the rapid topochemical destructive sorption reaction occurred. As the vanadium concentration was increased, the time for reaching the active state decreased.

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Oxidative dehydrogenation of hydrocarbons on supported vanadium catalysts: the influence of catalyst support nature

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Styrene and propylene are important monomers in chemical industry. Propylene is usually extract from petroleum refining gases or produced by the dehydrogenation of alkanes on Cr_2O_3/Al_2O_3 catalysts. Styrene is also produced by the dehydrogenation of ethylbenzene on potassium promoted Fe_2O_3 catalysts. However, despite the high yield of the product, this process has many disadvantages such as catalyst coking and need to carry out the process in the presence of superheated steam. Alternative way of the production of styrene and propylene is oxidative dehydrogenation of ethylbenzene and propane on V_2O_5/MgO [1], $V_2O_5/CeO_2/Al_2O_3$ catalysts [2].

The purpose of this work is to study the influence of the catalyst support nature on the catalytic activity of supported vanadium catalysts in the oxidative dehydrogenation reaction of propane and ethylbenzene.

The samples of the catalysts – VO_x/SiO_2, VO_x/TiO_2, VO_x/Al_2O_3 and VO_x/AlC – were synthesized by the impregnation method using an aqueous solution of ammonium metavanadate. SiO_2, TiO_2, γ-Al_2O_3 and carbon-modified γ-Al_2O_3 (AlC) were used as a catalyst support. The catalysts were characterized by low temperature nitrogen adsorption, XRD and TPR techniques. Catalytic activity of the samples in the oxidative dehydrogenation reaction was determined on a flow catalytic installation with online chromatographic analysis of the products.

According to XRD data, VO_x/Al_2O_3, VO_x/SiO_2, VO_x/TiO_2 catalysts contain only phases of the corresponding support (γ-Al_2O_3, amorphous SiO_2 or anatase) and orthorhombic V_2O_5. VOx/AlC contains a phase of graphite along with γ-Al_2O_3 and V_2O_5. The phase of V_2O_5 is well crystallized in both VOx/TiO_2 and VOx/AlC samples, with the mean crystallite size being 40 nm. VO_x/SiO_2 and VO_x/Al_2O_3 samples contain V_2O_5 phase in dispersed state. According to TPR data, the formation of different forms of vanadium oxide on the catalyst surface is observed. VO_x/TiO_2 sample is characterized by two peaks of hydrogen consumption. Those are weak peak at 360-530ºC and intense one above 550ºC. TPR profile of VO_x/SiO_2 also contains two peaks those are weak peak at 200-450ºC and intense one above 450ºC. VOx/AlC and VO_x/Al_2O_3 samples are characterized by only one peak of hydrogen consumption with maximum at 595ºC and 536ºC, respectively.

According to the catalytic data, VO_x/Al_2O_3 sample are the most active and selective among samples studied, with its selectivity on propene being 41% at propane conversion of 23%. The VO_x/AlC sample show comparable selectivity on propene (39%) at the same propane conversion. The lowest activity (propane conversion of 23%) and selectivity on pronene (30%) were demonstrated by VO_x/SiO_2 sample.

Thus, the use of different supports leads to the change in activity and selectivity of the catalysts in oxidative dehydrogenation of hydrocarbons due to the formation of different forms of vanadium oxide on the catalyst surface depending on the nature of the used support.

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SECTION 3:
Industrial implementation of catalytic processes

Перспективы каталитического окисления кумола в промышленности

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Окисление изопропилбензола является наиболее важной стадией совместного получения фенола и ацетона, так как именно на этой стадии образуются целевой продукт (гидропероксид кумола – ГПК) и ряд побочных продуктов (диметилфенилкарбинол, ацетофенон и т.д.), снижающие эффективность производства. Для ускорения процесса окисления кумола различными исследователями были предложены каталитические системы. Однако до сих пор в промышленности процесс ведется без использования катализатора. Проблема каталитического окисления кумола заключается в том, что известные каталитические системы действительно увеличивают скорость окисления, однако не обеспечивают приемлемой селективности превращения кумола в гидропероксид на стадии окисления, и кроме того, способствуют неконтролируемому разложению ГПК на стадии его укрепления. Последнее обстоятельство может привести к тепловому взрыву, что имело место в некоторых производствах.

Однако исследования показали, что некоторые производные N-гидроксифталимидов являются высоко активными и селективными катализаторами образования гидропероксидов, в т.ч. ГПК, что открывают новые возможности интенсификации данного процесса в промышленности. Предложенные нами катализаторы лишены тех недостатков, о которых говорилось выше, практически не разлагают ГПК, позволяют в разы увеличивать скорость его накопления, что в итоге приводит к высокому съему продукта и снижению потери ГПК на стадии укрепления его раствора. Таким образом, появляются возможность значительного увеличения производительности промышленных реакторов, и разработать в дальнейшем новые высокоэффективные, малогабаритные реакторы окисления.

Необходимо отметить, что более 60 % энергозатрат совместного производства фенола и ацетона приходится на долю стадии укрепления оксидата, где концентрация ГПК увеличивается с 22 ± 3 до 89 ± 1 %, с которой возвращают непревращенный кумол. Если концентрацию ГПК в оксидатеувеличить до уровня 40% при сохранении приемлемой селективности (более 90 %), чего позволяет использование производных N-гидроксифталимида, то нагрузку на узел ректификации можно уменьшить на величину разности количества ГПК, и таким образом значительно снизить энергоемкость производства фенола.

Если производство оксида пропилена базировать на ГПК, то вовсе можно исключить стадию ректификации оксидата, а полученный оксидат использовать для эпоксидирования пропилена или других олефинов. Такая схема обеспечит высокую селективность процесса окисления кумола (за счет уменьшения количества ингибиторов с возвратным кумолом), низкие потери ГПК на стадии укрепления и энергоемкости. Отмывке будет повергаться только поток, конденсированный из отработанного воздуха, что значительно уменьшит образование сточных вод, потери ГПК в виде натриевых солей с химически загрязненной водой.

При каталитическом окислении кумола увеличение конверсии кумола до 35-40 % за проход приведет к выделению большего количества тепла. Поэтому существующие реакторы должны быть переоборудованы теплообменниками с большой поверхностью или изготовлены реакторы новой конструкции для обеспечения эффективного теплосъема и высокой производительности. Теплота реакции окисления в реакторах (в секциях) может быть использована для нагрева кумольной шихты, подаваемой в змеевики реактора. Для повышения безопасности окисления, охлаждение водой и шихтой должно чередоваться от секции к секции, что, с одной стороны, облегчит установление нужного температурного профиля, а с другой – уменьшит расход воды и затраты на ее подготовку и транспортировку.

Для подтверждения эффективности предлагаемых вариантов модернизации нами разработана компьютерная модель узла окисления действующего производства и принята как базовая технология. Определены технико-экономические показатели производства по сравнению с используемой технологией.

Предлагаемый способ окисления кумола может быть реализован с учетом специфики предприятий, производящих фенол и ацетон, с минимальной переделкой или заменой имеющего оборудования. На базе усовершенствованного процесса можно осуществить реализацию проекта оксида пропилена, т.е. организовать более гибкое производство: совместного получения фенола, ацетона и оксида пропилена или как разновидность наряду с этими ценными продуктами получать и α-метилстирол. Основные стадии данного процесса отработаны на модельных установках, однако есть необходимость осуществить полную отработку технологии на пилотной установке и провести ее оптимизацию.

Разработка каталитического окисления кумола представляет интерес для производителей фенола и ацетона, таких как ОАО «Казаньоргсинтез», ОАО «Уфаоргсинтез», ОАО «Самараоргсинтез» (Холдинг САНОРС), ОАО «Омский каучук» и ОАО «Саратоворгсинтез» (приостановил производства), которые по сей день используют морально устаревшую и малоэффективную технологию. Отработка предлагаемого способа на пилотной установке позволила бы ускорить ее реализацию в промышленном масштабе. Таким образом, есть все основания считать востребованным предлагаемого проекта для промышленности страны, которого можно реализовывать совместно с крупными предприятиями в т.ч. в рамках НИОКР и грантов.

Investigation of the activity of hydrotreating catalysts diesel fuel fraction Surgut condensate stabilization plant

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Surgut plant condensate stabilization by V.S. Chernomyrdin

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At present, Russian refineries migrating to the diesel fuels that meet the technical regulations "On requirements for automobile and aviation gasoline, diesel and marine fuel, jet fuel and heating oil" Class 5 environmental standard [1].

The main regulated parameters such fuels are high cetane number (at least 51), low sulfur content (not more than 10 ppm) and polycyclic aromatic hydrocarbons (less than 11% wt.). [2]

In order to achieve high quality and reducing the share of the total sulfur diesel fuel derived from oil, gas and raw materials north of the Tyumen region, studies were carried out four brands of catalysts produced by the leading Russian and foreign companies.

The test materials were a fraction of diesel hydrotreater Surgut Condensate Stabilization Plant OOO "Gazprom Recycling" boiling range 180-340 °C.

The most efficient in the process of hydrotreating catalyst KGSH-08 NPF "Olkat", the active component of which is an oxide of nickel (II).

Subject catalyst brand of heavy tires-08 showed not only high catalytic activity in reactions girogenizatsionnogo desulphurization, but also will significantly reduce the temperature at the outlet of the hydrotreating reactor.

Catalytic KGSH-08 is characterized by long life, especially in the case of raw material, which is a gas condensate mixture with a relatively low content of harmful catalyst poisons.

In general, in the world there is a gradual transition from aluminum-cobalt-molybdenum to aluminum-nikel-molybdenum hydrotreating catalysts.

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A two phase single piston external combustion engine for CHP applications

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A crucial aspect of the practical realisation of thermodynamic cycles (e.g. Carnot, Joule, Rankine, Stirling) for power generation relates to the processes of heat transfer from a source of heat (almost invariably from the combustion of fossil fuels) to the working fluid, during the heat addition stage of the cycle [1]. Therefore, the intensification of these processes is essential for the improvement of the efficiency and power density of the resulting heat engines. To address this challenge we are investigating the use of suitable catalysts with good thermal conductivity for uniform heat transfer to the working fluid within the engine.

These catalysts are developed for use with a particular, new type of two phase single piston external combustion engine (i.e., featuring periodic evaporation and condensation of the working fluid), which is predicted to have a relatively inexpensive design and a high efficiency and power density. The early concept of this engine presented in [2]. This engine featuring our prepared catalyst is envisaged for use, for example, in the development of energy-efficient CHP plants. Such a scheme is expected to be widely applicable in the industrial, commercial and even domestic/residential sectors, in order to allow improvements in overall energy efficiency, primary fuel usage minimisation, as well as noise, vibration and emission reductions.

Specifically, the direct combustion of hydrocarbons and oxygenated fuels for energy production can be inefficient because these processes induce high temperatures and emissions [3]. A two-step catalytic process featuring synthesis gas production from various fuels and its subsequent feeding to engines for power generation is a promising alternative. An essential advantage of this approach is that the engine runs on the normalised fuel (synthesis gas), which allows higher engine efficiencies and lower emissions of NO_x, CO, CO_2. Suitable catalysts are being designed for this fuel conversion to the synthesis gas in order to optimise the two-step heat generation process. Further, catalytic heat-exchangers are crucial for waste heat utilisation in order to further improve the efficiency of designed cogeneration systems to ensure their competitiveness in the market of electricity suppliers.

This work was performed under the theme "Thermodynamic power generation cycles for improved energy efficiency" of the UNIHEAT project [4]

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Kinetic Model of Diesel Fuel Catalytic Hydrodewaxing Process

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The most important cold-flow properties of diesel fuel are pour point, cloud point and cold-filter plugging point [1]. Solid phase which sediments in diesel fuel at low temperatures is a complex mixture consisting of paraffin hydrocarbons different structures and molecular weight. Hydrocarbons with asymmetric branched structure are characterized by low crystallization temperature and in some instances are absolutely not capable to crystallize. The cloud point of diesel fuel increases sharply even if small content of n-paraffins C_{20}–C_{26} is present.

Reduction of diesel-fuel pour point is achieved by means of hydrodewaxing process, which basis on two main reactions: hydrocracking and hydroisomerisation of high molecular weight linear paraffins C_{10}–C_{27} over bifunctional Ni-Mo catalyst [2]. During the process sulfur-, nitrogen- and oxygen containing compounds and aromatic hydrocarbons hydrogenation occurs over Co-Mo catalysts as well.

The aim of the present work is diesel fuel hydrodewaxing process kinetic model development for optimization of technological parameters.

Since the catalytic hydrodewaxing process is an advanced cracking process of crude oil, the thermodynamic parameters for high molecular weight hydrocarbons have not been found in a directory. That is why, quantum-chemical methods, realized in software Gaussian, have been used for the thermodynamic properties of hydrocarbons estimation. The DFT (Density Functional Theory) method, the B3LYP model as theoretical approximation, and basis 3-21G has been adopted for calculations. It has been found that hydrogenation reactions of polyaromatic to mono-aromatic compounds, isomerization of n-parafins, hydrogenation of mono-aromatic compounds to naphthenes, and hydrogenation of olefins to n-parafins are reversible, while paraffins C_{10}–C_{27} hydrocracking pass only in forward direction.

As a result of thermodynamic analysis with taking into account condition of reaction reversibility and aggregation of hydrocarbons in groups by chemical features the formalized hydrocarbons conversion scheme of the hydrodewaxing process has been created. According to the created formalized hydrocarbons conversion scheme, kinetic model of hydrodewaxing process has been developed. It is a differential equation system of reactants concentrations changing by contact time with the following initial conditions: $\tau=0$, $C_i=C_{i0}$.

Kinetic parameters of hydrodewaxing process reactions determination involves the estimation of pre-exponential factors in the Arrhenius equation via minimization differences between calculated and experimental hydrocarbons concentrations in the product and reactions rate constants calculation. The initial approximations of reactions activation energies have been selected according to the literature data. Hydrocracking, dehydrogenation of n-paraffins C_5-C_9, and hydrogenation of olefins to isoparaffins pass with the greatest speed, which is in agreement with theoretical, experimental and thermodynamic regularities. Rate constants of these reactions at temperature 355 °C are 1.090, 1.666, 2.920 $l\cdot s^{-1}\cdot mol^{-1}$ respectively. Kinetic model is formalized and quasi-homogeneous, therefore the reaction rate constants are effective, i.e. they are the combination of all intermediate stages constants.

Estimation of the technological parameters influence has been investigated using created computer modelling system. Thus, when the temperature is 380 °C, hydrogen/feedstock molar ratio is 3,3:1,0, and pressure is 6.79 MPa, the conversion level of n-paraffin hydrocarbons in hydrocracking reactions is 64 %.

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SECTION 4:
Analytical support of catalytic technologies

Separating multicomponent lipid complex of CO_2-extract based on silicones

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Currently great significance is attached to the quality of produce presented at the market. Therefore efficient quick, fast non-labor intensive relatively cheap methods of checking the quality of the produce which producers manufacture are of great importance for them.

The urgency of utilizing extracts on food industry lies in increasing produce quality which consequently brings about success in the market. In the modern world demand for wholesome natural products is growing. And as nowadays there are no plant extracts which are more natural than CO_2-extracts, the produce into which composition they are incorporated may receive great popularity among consumers.

The object of this work is utilizing the method of thin layer chromatography for identifying individual substances of the investigated CO_2-extract.

The problem of identifying multicomponent composition of extracts, the degree of extracting biologically active substances has not been solved by now. The issue of fast and exact determining the quantitative and qualitative analysis of the composition of CO_2-products extraction was investigated by many scientists, including the scientists of department of essential oils technology the KubSUT. The conditions for maximally possible separating extract constituent’s essential oil raw material when chromatographic method is carried out, have been developed. This technique may be employed at the laboratories of the enterprises connected with investigating the quality and certifying the raw material of plant extracts as well as at the scientific-research institutes and educational institutions.

The basic peculiarity of the thin layer chromatography method is the eluent a solvent or solvent system providing separation movement along the layer of sorbent (porous material capable of absorbing the substance as the result of sorption) at the expense of capillary forces, this representing the simplicity and ease of carrying the analysis out.

One of the most acceptable for us is the produce of JSC Sorbpolimer. They provide us with highly efficient plates of sorbfil brand on polymer or aluminum base which ensure high quality and accurate results of carrying out the method of thin layer chromatography for identifying individual substances of the investigated CO_2-extract.

The method of thin layer chromatography for checking CO_2-extracts quality includes the following main stages: plate preparation, sample preparation, chromatographic chamber preparation, sample laying chromatography process, eluent evaporating from the plate, plate development its fixing, identifying, quantitative assessment.

It is possible to distinguish the following basic advantages of the thin layer chromatography method: oil the constituents of the sample remain in the sorbent layer, the achieved sample separation is easy to be evaluated visually, it is simple to the sample purity, it is possible to store the plates with the separated samples, we may employ computer facilities for optimizing the analysis, if the work is organized it is possible to assess the results quantitatively, the assessment being high-quality and exact one.

The presented technique makes it possible to quickly and with high quality the component composition of the extracts as well as to present visually the spectrum of the sequence of extracting biologically active substances and their mass share in finished product in CO_2-extracts.

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Metal nanoparticles modified carbon electrodes for organic compounds analysis

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Carbon electrodes are often used as substrate electrodes in electrochemical analysis, since they have wide operating potential window, high resistance to aggressive media and also their cost is sufficiently low. However, this type of electrodes has quite low sensitivity and the lack of selectivity at voltammetric analysis of organic compounds. Different modifiers are introduced on the electrodes surface to solve said problem.

It is well-known, that gold and platinum group metals are versatile catalysts for many electrochemical reactions [1]. Catalytic properties of metal particles on the electrode surface are largely determined by their size, shape, dispersion, the nature of the substrate, the nature of the precursor (the ion metal form), the surface state and the method of introduction of the modifier [1]. In all cases, when organic compounds are used during the modification process, the change in electrochemical response of nanoparticles or the electrode substrate may take place [2]. That is why the development of methods of carbon electrodes modification by metal nanoparticles in the absence of organic agents (stabilizers, fixing agents, etc.) is an urgent task. In present work it is proposed to use stable nanoparticles dispersions obtained by laser ablation of bulk metallic targets in pure liquids [3] as modifier's source. Carbon electrodes modified by metal nanoparticles (Au, Pt, Pd, Ni, Cu, in general size from 2-3 to 20 nm and up to 70 nm for Pd, about 180 nm for copper) from its ethanol dispersions (0.1 g/l) were investigated. Introduction of modifiers was conducted by keeping electrodes in ethanol dispersions of metal nanoparticles within 10 minutes with subsequent air drying at room temperature and rinsing in distilled water. For electrodes activation a single potentials scan from -1.5 to +2.5 V in the background electrolyte with the rate of 30 mV/s was conducted.

The appearance of electrochemical oxidation peaks of ascorbic acid, adrenaline and glucose and the peaks shift for dopamine and hydroquinone on modified electrodes indicates that these metal nanoparticles exhibit catalytic activity in organics electrochemical oxidation.

Also it was found that Cu nanoparticles on glassy carbon electrode surface allow ascorbic acid and dopamine peaks differentiation (non-modified glassy carbon electrode shows only one well-defined peak). Therefore, using Cu-modified GCE it is possible to determine ascorbic acid and dopamine in their simultaneous presence.

Thus, it may be concluded that Au, Pt, Pd, Ni and Cu nanoparticles obtained by laser ablation of metals in liquid can be used as modifiers of graphite electrodes for organic compounds analysis via voltammetry.

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Distribution of active surface centers (DAC) spectroscopy and catalytic properties of solids

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Recently distribution of active surface centers (DAC) spectroscopy is actively applied to study acid-base properties of solids. Method is based on measurements of selective adsorption of acid-base colorimetric indicators with different values of pKa (logarithm of dissociation constant). This method is based on L.P. Hammet's concept that the interaction of acid-base indicators with functional groups of solids proceeds with equal ratios between the activities of ionic and molecular forms of the indicator. The content of different sites, their distribution according to the ionization/dissociation constants and acidity can be measured using the adsorption of acid-base indicators with different intrinsic pKa values as described by K. Tanabe [1]. Further method was advanced by Professor A.P. Nechiporenko and successfully used by her pupils and other scientists.

Surface characteristics of solid influences interface interaction in which this solid participates. Efficient approach to consider such interactions is to view them as acid-base ones, since acid-base interactions determine adsorption and bonding of organic molecules to solid surface. This means that surface of solid particle have certain active centers (defects, functional groups) possessing electron donor or acceptor properties thus having Lewis base or acid properties; and centers with proton donor or acceptor properties thus having Broensted base or acid properties.

In research of our team method was applied to study surface properties of components of polymer composites [2], luminescent materials, catalysts, gas sensors, proton membranes and it was shown that their functional properties strongly depend on distribution of acid-base active surface centers. Several methods were utilized to control those distributions in order to improve functional properties of materials: plasma treatment, electron beam and gamma-ray irradiation, core-shell approach as well as hydration and heat treatment [3].

One example is 10%NiO•7%CeO_2•3%BaO•80%Al_2O_3 catalyst which was synthesized using a slurry process. It was shown that electron beam irradiation of catalyst provided up to ~ 2 times increase of its activity (at 90-100°C) in hydrogen oxidation. The comparative analysis of the obtained data indicates that the catalyst activity of the studied samples evidently grow with the content of Broensted acid adsorption centers with pKa 2.1(μmol/m^2).

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