CATALYSIS:
from science to industry

PROCEEDINGS OF VII INTERNATIONAL SCIENTIFIC
SCHOOL-CONFERENCE FOR YOUNG SCIENTISTS

October 11-15, 2022
Tomsk State University, Tomsk

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

CATALYSIS: FROM SCIENCE TO INDUSTRY

Proceedings of
VII International scientific school-conference for young scientists

October 11-15, 2022

Tomsk 2022

UDC 544.47/544.72+661.7
LBC 24.54
C30

C30 **Catalysis: from science to industry:** Proceedings of VII International scientific school-conference for young scientists “Catalysis: from science to industry” / Tomsk State University. – Tomsk: TSU Publishing House, 2022. – 177 p.

ISBN 978-5-907572-26-3

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

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The Scientific School for Young Scientists “New catalysts and catalytic processes to solve the challenges of environmental responsible and resource-saving energy production” organized within a project supported by the Russian Science Foundation was held during the 6th International School-Conference for Young Scientists “Catalysis: from Science to Industry”

INFORMATION SUPPORT
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ИНЖИНИРИНГОВЫЙ ХИМИКО-ТЕХНОЛОГИЧЕСКИЙ ЦЕНТР

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

2500 м²	технологическая площадка
100+	партнеров-ученых
60+	технический и управленческий персонал
70+	организаций-партнеров
400+	контрактов за 8 лет
30+	технологий внедрено

ИНЖИНИРИНГОВЫЕ УСЛУГИ

Полный комплекс инжиниринговых услуг от идеи до промышленного внедрения. Масштабирование химических технологий Разработка технологической и технико-экономической документации. Сопровождение организации производства (авторский надзор, ЕМС, РМС).

ПАРТНЕРСТВО С ВУЗАМИ

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

ПРОФЕССИОНАЛЬНАЯ КОММАНДА

Более 60 высококлассных специалистов в области разработки и внедрения наукоемких химических и биологических технологий. Инженеры, технологи, ученые, маркетологи с опытом работы на ведущих химических предприятиях и в лучших вузах и НИИ России.

ДОСТУП К ЭКСПЕРИМЕНТАЛЬНЫМ И ОПЫТНО-ПРОИЗВОДСТВЕННЫМ ПЛОЩАДКАМ

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

СОБСТВЕННАЯ ТЕХНОЛОГИЧЕСКАЯ ПЛОЩАДКА С ОПЫТНО-ПРОМЫШЛЕННЫМ ОБОРУДОВАНИЕМ

- Синтез органических и неорганических материалов
- Синтез твердых форм катализов и сорбентов
- Переработка полимерных материалов
- Выпуск опытных партий продуктов
- Эксплуатация пилотных установок

НАШИ РЕШЕНИЯ

ИХТЦ — это новый взгляд на взаимодействие научных организаций и предприятий реального сектора экономики. Мы на реальных примерах показываем, как снизить риски и увеличить прибыль, сделать процесс трансфера технологий в химическую промышленность простым, понятным и выгодным всем его участникам.

НИР И НИОКР

Инжиниринговым центром заключено более 150 договоров на проведение научно-исследовательских и опытно конструкторских работ.
Мы объективно оцениваем возможности реализации бизнес-задачи и находим оптимальное исследовательское решение.

РЫНОЧНЫЙ АНАЛИЗ

Мы не делаем кабинетную аналитику. Мы посещаем предприятия, опрашиваем покупателей, импортеров и экспортеров.
Закладываем выверенные данные в систему и на выходе получаем точную и работающую маркетинговую стратегию.

ВНЕДРЕНИЕ И МОДЕРНИЗАЦИЯ

Мы делаем процесс внедрения и настройки тонких химических технологий на производстве простым, понятным и выгодным.
Специалисты ИХТЦ передают технологию как готовый лицензированный продукт, проводят пуск и наладку новых линий.

КАТАЛИЗАТОРЫ

Выполняем полный цикл постановки катализатора в производство: научную разработку, создание опытной установки/линии для синтеза необходимой производительности, проведение испытаний, масштабирование процесса и внедрение на производство.

МОДЕЛИРОВАНИЕ

Математическое моделирование заметно снижает затраты и время на внедрение разработок или оптимизацию действующих процессов. Компьютерная модель готова для проверки на модельной установке или сразу на производстве.

АУДИТ И ОПТИМИЗАЦИЯ

Специалисты Центра имеют опыт проведения производственного аудита на ведущих предприятиях химической отрасли. Мы предлагаем услуги технологического и энергетического аудита с последующим консалтингом трех уровней проработки.

ПРОЕКТИРОВАНИЕ ПРОИЗВОДСТВ

Оказываем весь комплекс услуг по разработке исходных данных на производство (ИДП), открытию дополнительных линий, составлению детального химического бизнес-плана и технико-экономического обоснования.

ОПЫТНОЕ ПРОИЗВОДСТВО

Оперативно разворачиваем и налаживаем опытное производство химических соединений, реактивов и реагентов, катализаторов, топливных присадок на заказ. Решаем широкий спектр задач по синтезу, очистке, получению специальных материалов.

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Altamira Instruments systems for catalyst characterization

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PLENARY LECTURES

Single atoms versus clusters in the Pt-CeO_2 system

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Platinum group metals (PGM) supported on metal oxides are among the most used catalysts for a wide range of oxidation reactions. PGM (Pt, Pd, Rh) are often combined with ceria as a catalysts for such reactions as CO oxidation, CO preferential oxidation, water-gas shift reaction and CO_2 hydrogenation. PGM and ceria are also essential components of three-way conversion catalysts (TWC) for the neutralization of automotive exhaust gases. The oxidizing ability of these catalytic materials is controlled by effect of strong metal–support interaction (SMSI). Due to this SMSI effect the state and structure of active species in PGM/CeO_2 catalysts are of key importance. These species can be 1) metallic nanoparticles (NPs)/clusters, 2) metal-oxide NPs/clusters and 3) neutral/ionic atomically dispersed species on the ceria surface. Besides, the formation of substitutional solutions and/or joint nanodomain phases of PGMs and reducible oxides as ceria is also well documented. Thus, even in simple metal oxide catalysts as Pt-ceria, various forms of the active component are present due to the realization of the SMSI effect. In this regard, the establishment of the catalytic characteristics of individual forms of metals on the surface of cerium oxide is a basic task in the development of new efficient catalysts. Metal nanoparticles (NPs), even highly dispersed ones, are not the most cost-efficient form of platinum for the generation of surface active sites. It is more beneficial to place atomically dispersed active component as single atoms (SA) on the surface of oxide supports. In this way the expensive platinum can be used to the maximum extent and significant promoting effects can furthermore be achieved due to SMSI.

In this presentation, the main attention will be paid to Pt/ceria catalysts due to the surface specificity of the platinum-ceria interaction. For Pt/CeO_2 catalysts, main characteristic feature is the stabilization of Pt both in the ionic form of single atoms (SA) and clusters, in which platinum can be either metallic (Pt^0) or completely oxidized (PtO_x). The role of SA and PtO_x in low-temperature activity of Pt/CeO_2 catalysts was considered. It was recently established that the combination of platinum and ceria creates very efficient catalysts with capability to oxidize CO at room temperature and below. This finding was designated as abnormally low-temperature CO oxidation (ALTO CO) on the Pt/CeO_2 catalysts. It has been established that SA-sites cannot provide high catalytic activity; the specific oxidized PtO_x clusters are responsible for ALTO CO.

The combination of catalytic, spectroscopic and microscopy experimental methods together with density-functional theory calculations is used for the investigation of the transformation of SA and reduced Pt species into PtO_x clusters and the implications for the activity of these catalysts below room temperature. The elucidation of the conditions at which oxidation to PtO_x clusters happen, the description of the differences in redox behavior for catalysts with either high or low Pt loadings will be considered in this presentation.

Finally, the modeling of CO oxidation kinetics on Pt/CeO_2 catalysts in a wide temperature range was discussed. Using the catalysts with the active SA centers a satisfactory simulation of CO conversion at temperatures higher than100°C was carried out based on the concepts of the Mars-van Krevelen (MvK) mechanism. To simulate the reaction kinetics in the temperature range below 100°C, the Pt-O-Pt active centers based on PtO_x cluster forms were considered. The introduction of PtO_x cluster forms into the kinetic scheme made it possible to consider both the MvK and concerted Low-T mechanisms for modeling of the CO oxidation kinetics over the entire temperature range of the reaction from –50°C to 450°C.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the governmental order for Boreskov Institute of Catalysis (project AAAA-A21-121011390053-4) and Russian Science Foundation grant #21-13-00094 from 20.04.2021.

MOFs – water adsorbents for energy related applications: from test-tube to practical realization

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In recent years, a rapidly growing population, the growing energy demand, and environment pollution, caused by the extensive use of fossil fuels, have inspired considerable research interest to renevable energy related applications, among which there are Adsorption Heat Conversion (AHT) and Water Harvesting from the Air (AWHA). These technologies offer effective utilization of low-grade solar or waste thermal energy for cooling, heating, and potable water production with low environment impact. AHT and AWHA are based on reversible adsorption of water vapor on an adsorbent, with following thermally driven desorption. A keystone for the successful implementation of these technologies is the properties of the adsorbent. Metal–organic frameworks (MOFs) are a novel family of crystalline compounds that are commonly constructed by metal ions or metal clusters coordinated with polydentate organic ligands forming frameworks with ordered structures [1]. Owing to their high adsorption capacity and the possibility of target-specific design MOFs hold great promise for these applications. Among the existing porous solids, MOFs stand out by their unprecedentedly high porosity and specific surface area, large adsorption capacity, variable hydrophilicity, etc. One of the most important advantages of MOFs is the possibility to control and rationally adjust the adsorption properties by modifying their structural and functional elements stemming from the principles of reticular chemistry [2]. This has resulted in a huge variety of the porous structures of MOFs with diverse adsorption behavior and, as a consequence, different types of water adsorption isotherms [3]. That makes it possible to select, or even intently design the MOFs with the properties matching the climatic conditions of the specific region. In this work, first, the principles of AHC and AWHA are described, the specific features of adsorbents needed for AHC and AWH are defined, and promising MOFs are considered. The types of isotherms of water adsorption on the MOFs and mechanisms, associated with them are discussed. The available tools for rational design of MOFs with required properties are described. Several challenges to be solved, namely, low hydrothermal stability of MOFs, high cost, and complicated synthesis, strategies of MOFs shaping as granules or thin films are viewed. Finally, some perspectives on advanced MOFs promising for continuously-operating and scalable AHT and AWH systems are provided.

This work was supported by RSF Grant n. 22-23-00659.

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Photocatalytic hydrogen production and CO_2 reduction over g-C_3N_4-based photocatalysts

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The annual increase in energy consumption and the reduction in the reserves of fossil carbon-containing raw materials necessitate the development of new types of renewable energy sources. The areas of alternative energy based on the use of solar energy have paramount scientific significance and, in the future, significant practical prospects. The total amount of solar energy reaching the Earth annually is 3×10^{24} J/year, which is about 10000 times the current total energy consumption worldwide. The process of photocatalytic production of hydrogen under the visible light irradiation is considered to be especially attractive in this area, since in this case the transformation of solar energy into the energy of chemical bonds is carried out [1].

The unique properties of hydrogen make it possible to consider it a universal and most environmentally friendly chemical energy carrier, suitable for use in almost all types of heat engines and many other types of power generating devices. From this point of view, the development of new efficient technologies for hydrogen production is relevant for solving, at least, local problems of hydrogen energy [1]. Also, today, humankind faces the problem of utilization of greenhouse gases, especially CO_2. CO_2 could be converted to more reactive compounds, such as CO and CH_4 by means of photocatalysis using renewable sources: light, CO_2, and water [2].

The main factor hindering the practical use of photocatalytic processes such as hydrogen production and CO_2 reduction is the lack of efficient and at the same time stable heterogeneous photocatalysts functioning under the visible light irradiation, which makes up about 43% of the solar spectrum. Recently, more attention of researchers has been attracted by the graphitic carbon nitride g-C_3N_4. This material has the properties of a semiconductor with a band gap of 2.7 eV, and the positions of the valence and conduction bands are suitable for the photocatalytic water splitting and CO_2 reduction. Traditionally, g-C_3N_4 is synthesized by thermal condensation of nitrogen-enriched organic precursors – cyanamides, melamine, and urea. Nevertheless, the photocatalytic activity of g-C_3N_4 synthesized by this method is usually low due to the rapid recombination of photogenerated electron-hole pairs. Various approaches are being developed to increase the activity of photocatalysts based on g-C_3N_4. The main strategy here is to create systems with interphase heterojunctions. So, recently, for the complete water splitting, such composite systems as CdS/g-C_3N_4, TiO_2/g-C_3N_4, $BiVO_4$/g-C_3N_4 and CoO/g-C_3N_4 have been proposed [3]. Also, the synthesis of g-C_3N_4 with the use of various templates for obtaining materials with a developed porous structure has found wide application.

This lecture systematizes data on the approaches applied to the synthesis of graphite-like carbon nitride at the Boreskov Institute of Catalysis. In particular, such synthetic approaches as the creation of heterostructures, the deposition of cocatalysts, and various template synthesis techniques will be considered. The relationship between the characteristics of synthesizing g-C_3N_4 and its activity in the targeted processes of hydrogen production and carbon dioxide reduction will be discussed.

This work was supported by Russian Science Foundation Grant 21-13-00314.

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Thermally-stable heterogeneous single-atom catalysts

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Catalysis has been in the era of the precise design and manipulation of catalyst structure in the atomic scale for developing highly efficient catalysts. Single-atom catalysis has attracted extensive attention since it was proposed in that it can bridge the gap between homogeneous catalysis and heterogeneous catalysis [1]. Because of the high atom efficiency, single-atom catalysts (SACs) have therefore attracted ever-increasing attention from numerous fields including material science, catalysis and electrochemistry. However, most of the catalytic reactions reported were carried out at relatively low reaction temperatures (< 100 °C) and catalytic reactions performed at temperatures of > 200 °C, such as dehydrogenation and reforming, are rarely reported since metal SACs are thermodynamically unstable and are prone to agglomerate at elevated temperatures due to Ostwald ripening (OR).

Metal SACs must keep stable during chemical reactions under industrial conditions, including at elevated temperatures [2]. Especially, in the transition from the academic curiosity to an industrially relevant technology, the thermal stability of metal SAC became much more important. Previous work has indicated that metal SACs prepared by atom trapping (AT) can withstand the temperature up to 800 °C in oxidizing conditions. However, many metal SACs are not stable under reaction atmospheres or at elevated temperatures. These SACs have been demonstrated to agglomerate to form nanoclusters due to the high free energy of SACs under reaction conditions. For example, atomically dispersed metal atoms can rapidly agglomerate to metal clusters or nanoparticles under catalytic reactions (CO oxidation, hydrogenation and dehydrogenation). Moreover, the size of Pt particles formed from single atoms on a Pt/Al_2O_3 increases with the reaction temperature from 150 to 325 °C, indicating that Pt species undergo dynamic structural transformation during reaction. Therefore, the development of metal SACs that are stable under reaction conditions is pivotal, which is prerequisite for future commercialization of these catalysts.

In this lecture, I will discuss the progress on the preparation and activation of thermally-stable single-atom catalysts (TSSAC) in catalysis. We firstly introduce atom trapping (AT) [3] and vapor-phase self-assembly (VPSA) to prepare thermally stable single atom catalysts, including on the supports of ceria (CeO_2) and $MgAl_2O_4$ [4]. The ceria represents the supports with strong metal-support interaction, while the $MgAl_2O_4$ represents the supports with weak metal-support interaction. We also describe two approaches to tailor the coordination structure of the Pt single atoms on the thermally-stable Pt_1/CeO_2 catalyst. Finally, the atom-trapped Pt_1/CeO_2 SAC can be used to load a second metal atoms to generate two-dimensional metal oxides which shows superior catalytic reactivity than three-dimensional metal oxides [5]. For the general and comprehensive understanding of SAC or TSSAC, such as support choices or carbon-supported SAC, the readers are referred to other important review articles.

This work was supported by the National Natural Science Foundation of China (22072118) and the Science and Technology Projects of Innovation Laboratory for Sciences and Technologies of Energy Materials of Fujian Province (IKKEM) (HRTP-[2022]-3).

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Template methods for controlling the structure and texture of ceria-based oxide catalysts

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Porous oxide materials are applied in many fields, such as electronics, separation processes, energetics, biotechnology, and catalysis. Among various metal oxides, porous cerium dioxide and complex ceria-based systems are the most used as catalysts or as non-inert supports for a wide range of catalytic reactions. These materials are known by their relatively low cost and toxicity, high thermal and chemical stability, and unique physicochemical properties related to the chemical composition and fluorite crystal structure. Facile transfer between cerium oxidation states, high concentration of oxygen vacancies and other defects, high oxygen storage capacity and oxygen ion conductivity provide their excellent catalytic properties.

Template methods are increasingly used in the synthesis of catalysts. The use of organic, inorganic, or biological materials as templates makes it possible to optimize the texture and morphology of the resulting systems. Thus, it is possible to achieve a narrow size distribution of pores in the required range, or, conversely, create hierarchical porous structures. It is less known, that the use of template has also a significant effect on the structural properties of produced materials: phase composition, crystallinity, and defectiveness. These structure features are crucial for catalytic performance of ceria-based oxide catalysts and provide the way of tuning their oxygen mobility.

This lecture, based on recent literature and own investigations, will provide overview of the factors, which determine the properties of ceria-based oxide catalysts during template synthesis. The nature of the template largely determines the synthesis conditions and the properties of the final materials. Wide opportunities are provided by the use of biological templates of a diverse nature, from widespread ones, for example, sawdust or cellulose, to exotic ones, for example, viruses, bacteria or their exoskeletons [1]. The lecture will systematize the types of templates and analyze the advantages and disadvantages of biotemplates in comparison with organic ones. Other factors affecting structural and catalytic properties are the nature of precursor salts, the conditions of template synthesis and subsequent calcination, which can be performed to remove or modify the template and crystallize catalytic precursors [2-4]. The influence of these features on the properties of final materials will be analyzed in the lecture as well.

A variety of template methods can be used to obtain materials with a uniform distribution of components, which ensures their close interaction and synergistic effects [5]. On the other hand, they make it possible, if necessary, to obtain materials in which one of the components of the desired degree of dispersion is distributed on the surface of the other component, ensuring the economical use and their availability for the adsorption and activation of reagents in various heterogeneous catalytic reactions. The main attention will be paid to the use of cerium-containing catalysts in oxidative catalysis reactions.

This work was supported by the Russian Foundation for Basic Research, project number 20-33-90065. The author acknowledge support from M.V. Lomonosov Moscow State University Program of Development.

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Computational modelling of bimetallic nanoparticles in catalysis

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Bimetallic nanoparticles (nanoalloys) often are materials of choice for many applications. However, determining chemical ordering in nanoalloys, which largely defines their properties, is very challenging. We developed a method to determine the lowest-energy chemical (atomic) orderings in nanoalloys by first-principles Density Functional Theory (DFT) calculations combined with a Topological approach [1,2]. The method allows one to reliably and efficiently predict the most stable ordering patterns of atoms in bimetallic crystallites with up to thousands atoms. So far the applications of the method have been focused to nanoalloys used in catalysis and energy technologies, for which the surface atomic ordering is key for the reactivity. Among the studied systems were catalytic bimetallic nanoparticles, such as PtCo [3,4], PtNi [5], CuNi [6], PdX [1,2] and PtX (X = Au, Ag, Cu) [7].

In this lecture the aforementioned computational method to model chemical orderings will be outlined and its applications will be illustrated by results obtained for catalytically-relevant bimetallic nanoparticles. The present modelling method is helpful for accelerating design of tailor-made bimetallic nanoalloys for various technological needs. It also allows deepening general understanding of the chemical bonding in nanoalloys.

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Environmental catalysis for VOCs pollution control and resource utilization

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In recent years, the total emission of volatile organic compounds (VOCs) in China has gradually increased. VOCs pollution emission has a prominent impact on the atmospheric environment, and is an important precursor for the formation of fine particles ($PM_{2.5}$) and ozone (O_3). VOCs pollution control is imminent and has become one of the priority directions of air pollution control in China. Compared with dust, SO_2 and NO_x pollution control, VOCs pollution control is still weak, and many aspects need further research, such as the urgent need to develop new catalyst preparation methods to improve the stability of low loading precious metal catalysts; to reveal the catalytic conversion mechanism of typical single and multi-component VOCs based on the typical exhaust gas composition emitted by specific industries.

Based on China's major needs in the field of VOCs pollution control, we have carried out systematic and in-depth research on the development of more stable, safer and more efficient catalytic oxidation technology for VOCs pollution control. It is found that lattice oxygen activity and VOCs adsorption are the key factors affecting the stability of noble metal single atom catalysts for catalytic purification of VOCs. Clarify the way to achieve the balance between lattice oxygen activity and VOCs adsorption by accurately regulating oxygen vacancy concentration or reduction pretreatment conditions, and obtain a stable and efficient noble metal single atom catalyst with low loading for catalytic purification of VOCs; Systematically studied the process of eliminating typical single and two-component VOCs with low loading Pt catalyst under complex working conditions such as the coexistence of H_2O, CO_2 or SO_2, proposed the mechanism of catalytic purification of VOCs mixed with toluene and acetone, and found that the key and stable intermediate species benzaldehyde oxidation is the speed control step of toluene removal. The interfacial effect of C-H bond highly selective breaking in alcohols VOCs is revealed, achieving highly selective catalytic oxidation of isopropanol to acetone under mild conditions, and opening a new way of VOCs resource utilization.

This work was supported by Natural Science Foundation of China (21622701, U1507108, and 21477005).

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KEYNOTE LECTURES

Solid-state NMR for in situ studies of hydrocarbon transformations catalyzed by metal-modified zeolites

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Light alkanes and alkenes being the products of natural gas and crude oil processing are available feedstock for producing valuable chemicals such as aromatic hydrocarbons, alcohols, and carboxylic acids. Owing to their unique properties, zeolites modified with the metals of 11-13 groups (Cu, Ag, Zn, Ga) are promising catalysts for light alkanes and alkenes aromatization [1-4]. For further development of the industrially relevant catalysts, fundamental research on the mechanisms of hydrocarbon transformations on metal-modified zeolites is needed, which will reveal the main reaction pathways and the roles of different active sites.

Solid-state nuclear magnetic resonance (MAS NMR) spectroscopy is a powerful tool for studying hydrocarbon activation and transformation on heterogeneous catalysts [5-8]. In this report, recent advances in the research of the activation and transformation of C_2-C_4 alkanes and alkenes as well as methane on Zn-, Cu-, and Ag-modified ZSM-5 and BEA zeolites are discussed. It is demonstrated that ^{13}C MAS NMR allows direct observation and identification of the surface intermediates formed on the catalysts during hydrocarbon reactions. The analysis of the evolution of the surface species during the hydrocarbon transformation enables the establishing of the reaction mechanism. ^{1}H MAS NMR can be applied to investigate a short-time process of C-H bond activation in alkane molecules via studying the H/D exchange reaction of the alkane with Brønsted acid sites of a zeolite. This report will provide interesting examples of the peculiarities of the H/D exchange of C_1-C_4 alkanes on metal-modified zeolites. It is also shown that ^{1}H MAS NMR can be used to monitor the kinetics of alkane conversion on through the pathways of aromatization and hydrogenolysis in situ and derive the kinetic parameters of the main reaction steps. Moreover, ^{13}C and ^{1}H MAS NMR data analysis reveals the possible involvement of methane in higher alkane conversion, which can aid in further applied studies in the field of methane utilization into useful products.

Having presented the selected data, we conclude that MAS NMR spectroscopy provides essential information for the development of industrial catalysts for light alkane and alkene conversion.

This work was supported by Russian Science Foundation (grant no. 21-73-10013) and the Ministry of Science and Higher Education of the Russian Federation within the governmental order for Boreskov Institute of Catalysis (project AAAA-A21-121011390053-4).

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N-Oxyl radical redox-organocatalysis in selective CH-functionalization

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The development of selective methods for CH-functionalization is one of long-term challenges in organic synthesis. It is the key to step- and atom-economical synthesis of value-added products from widely available hydrocarbon compounds with minimal negative environmental impact. Compared to most functional group transformations, CH-functionalization is harder to control due C–H bond inertness and the problem selectivity between different CH-fragments. Despite significant advances in the directing group assisted transition metal catalyzed CH-activation [1, 2] and carbenoid-complex mediated CH-functionalization [2], such processes have significant scope limitations and based mainly on homogeneous precious metal-containing catalysts. Thus, synthetically available, precious metal-free and recyclable photocatalytic systems for selective C–H functionalization are highly desirable.

Organocatalyzed free-radical CH-functionalization processes have recently got much attention in part due to discoveries in photoredox-catalysis and electrochemistry allowing to generate wide range of radical intermediates under mild conditions employing the energy of visible light [3] or electricity [4]. N-oxyl radicals represent the richest class of organic free radicals by the diversity of structures and applications, including CH-functionalization by selective hydrogen atom abstraction from an organic substrate by N-oxyl radical [5–8]. In the present work, a new type of catalytic system of mixed hetero-/homogeneous nature was developed for the selective alkylarene oxidation by molecular oxygen [9]. The proposed catalytic system consists of two widely available components: *N*-hydroxyphthalimide (NHPI, a homogeneous organocatalyst for free-radical chain reactions) and nanosized TiO_2 (heterogeneous UV-active photoredox catalyst). The interaction of NHPI and TiO_2 allows for a shift from UV to visible light photoredox activity and generation of phthalimide-N-oxyl (PINO) radicals that diffuse into the solution where NHPI/PINO-organocatalyzed free-radical chain reaction can proceed without the additional light input. Thus, single photocatalytic cycle can lead to multiple product molecules, which results in fundamental increase of catalytic activity. The NHPI/TiO_2 ratio controls the selectivity of oxidation affording preferential formation of hydroperoxide or ketone from alkylarene. Despite the proposed system contains homogeneous cocatalyst (NHPI), it is easily recyclable due to the low solubility of NHPI in non-polar organic solvents.

This work was supported by RSF Grant 21-13-00205.

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Application SAXS for the study of the ordered mesoporous materials

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Mesoporous materials such as SBA-15, MCM-41 and etc. are perspective for applications in the field of catalysis, adsorption, separation substances, template for nanomaterials, drug delivery systems and other applications due to their narrow pore size distributions and high surface area [1, 2]. Typical synthesis strategy of these materials based on the concept of ordered aggregation of surfactants in water media and covering these aggregates by silica layers with further calcinations for removing surfactant template [3, 4]. One of the noticeable drawbacks of these systems is less stability compared to the typical porous silica materials due to thin walls between porous. This stability also could be changed after impregnation and calcination of ordering porous structures by different compounds at the catalysts preparation. For study such materials traditionally used BET, TEM and X-ray diffraction. Last technique is often used to study the structure and ordering of porous matrices and their changes. Typical diffraction patterns are observed in small angle regions due to large distances of ordering. In this lecture reported methodical details of measurements and application of small angle X-ray scattering (SAXS) method for investigation of ordering to the porous structure and their changing at preparation supported catalysts on its base. For supported metal catalysts most parts of metal nanoparticles have limited sizes by the porous media. In the case of supported oxides, a silica matrix could be interacted with dopants and depending on the type of impregnated oxides porous silica matrix could be stable or shrink and destroy at calcination procedure. Also for the initial porous silica matrix it is shown that part of silica exists as non-porous amorphous particles and does not make an ordered porous structure. A new technique is proposed to determine non-porous amorphous silica in ordered mesoporous silica materials. This technique allows the determination of not only the amount of non-porous amorphous silica in a porous matrix, but also its particle size distribution.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the governmental order for Boreskov Institute of Catalysis (project AAAA-A21-121011390053-4) and FSUS-2020-0029.

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Study of Ag catalysts on Ce-Mn oxide for post-treatment of exhaust gases: state of the art and perspectives

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Nowadays, NO_x emissions remain the main problem of diesel engines [1]. The catalytic removal of NO_x ($DeNO_x$) can be performed using different technologies with advantages and disadvantages. Among the various methods, however, the one that is of greatest interest is the SCR (Selective catalytic reduction) system, in which the use of gas oil or hydrocarbons (HC)/oxygenated hydrocarbons, unburnt alcohols (HCO) as reducing agents, simplify the system and reduce costs, making these systems of particular interest, thanks, also, excellent performance of reducing and eliminating NO_x emissions from the exhaust diesel engine [2, 3]. In this study the role of Ag and Ag-Pt supported catalysts on oxides such as CeO_2, MnO_2 and mixed oxide such as $CeMnO_x$ was investigated in the selective catalytic reduction of NO_x [4, 5] using propene (C_3H_6) as reducing agents [3]. All the oxides, CeO_2, MnO_2 and $CeMnO_x$ (with molar ratio Ce/Mn = 1) were synthesized with the sol-gel method, using citric acid as a chelating agent (citrate method). The supports thus obtained were impregnated with aqueous solutions of $[Ag(NH_3)_2]NO_3$, in order to obtain catalysts with Ag loads of 1% and 0.5% by weight; while the bimetallic catalysts (Ag-Pt) containing 0.5 wt.% of Pt were prepared by impregnating the supports with acetone solutions of the precursor Pt $(Me_4N)_2[Pt_2(\mu\text{-}OH)_2(NO_3)_8]$). The calcination of the oxides was carried out at 500 °C for 3 hours, while the catalysts with Ag-Pt were calcined in air at 500 °C for 2 hours. To estimate the activity of NO SCR and the effects of the Ag and Pt, catalytic tests were performed using propene for HC-SCR, with a mixture composed of 1000 ppm in NO, 3600 ppm C_3H_6, 10 vol.% in O_2, 2.9 vol.% H_2 and He as balance gas, at WHSV of 25,000 ml g^{-1} h^{-1}. The physiochemical properties of the catalysts were obtained by several characterizations, such as XRD, XPS, H_2-TPR, N_2-physisorption and Raman spectroscopy.

This work was financially supported by the Ministry for Science and Education of the Russian Federation (Project No. 075-15-2021-1388) and by the Italian Ministry of Foreign Affairs and International Cooperation" ("Progettazione di Catalizzatori Attivi a base di Ag-Pt depositati su Ce e Mn modificati con Y per il Post-Trattamento dei Gas di Scarico emessi dai Motori Diesel" Prot. MAE01538512021-10-26).

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Silica and silica-based materials for sorption, catalysis and other applications

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Silica is a material widely used in many applications including sorption, chromatography, drying, storage, catalysis, production of polymer, tires, etc. The size of particles and/or granules, porous structure (including specific surface area, pore volume and pore size distribution) and surface concentration of silanols are the key characteristics of silica that determine its functional properties as an individual material or as a component in mixtures or composites. Silica is usually shaped as spherical granules with diameter of 4-7 mm or microspherical granules with sizes of 50-250 μm. Also, silica is used as a powder in some applications. In Russia, the problem consists in the limited production of silica. Granulated silica is produced by the Salavat Catalyst Plant (the Republic of Bashkortostan), while the production of powdered silica is rather low, and above 40,000 tons of silica are imported to Russia annually. Currently, the production of powdered and microspherical silica and silica-based materials is a challenge for the Russian industry.

The production of granulated silica (spherical granules) is based on the precipitation of liquid glass (nonstochiometric sodium silicate $Na_2O \cdot nSiO_2$) by H_2SO_4 combined with the shaping in column with organic oil. These types of silica are mainly used in gas- and petrochemistry as sorbents. Disadvantage of silica as a desiccant in comparison with alumina or zeolites is instability of granules in the presence of condensed moisture, the destruction of sorbent granules may lead to blocking of the sorption equipment. The development of water-stable silica is important to expand the application of silica as a sorbent. The synthesis of water-stable silica is based on the addition of powdered silica during the process of shaping of silica granules. This leads to the formation of hierarchical porous structure of granules and the decreasing of mechanic stress inside the granules that provide the water resistance.

The synthesis of powdered silica is rather important for tire industry because modern tires contain 25–40% of silica as a filler that improves the characteristics of tires and makes them more ecofriendly. This type of silica also can be produced by the precipitation of liquid glass by H_2SO_4 but without gelation process to keep the low bulk density and size of individual micropherical particles. The silica for tire production features moderate specific surface area (80–200 m^2/g) and wide mesoporous structure that is required for better distribution and bonding with the tire during the vulcanization process. Similar porous structure of microspherical silica characterizes silica used as a support for catalysts of ethylene and propylene polymerization. Wide mesopores are preferable for better contact with the polymers.

Powdered silica is used in food industry (as a sorbent for beer filtration), production of toothpastes, cosmetics, etc. However, the chemical purity requirements are higher for this silica. This type of silica can also be produced from the liquid glass, but the additional purification of the precipitate is required. If the chemical purity requirements for silica are high, the tetraethoxysilane (TEOS) can be used as a silica precursor.

The production of silica with ordered structure (MCM-41, SBA-15, etc.) with unique properties and high chemical purity can also be realized using liquid glass as a silica precursor. Thus, the production of inexpensive MCM-41 or SBA-15 becomes possible, and the application of these materials in sorption, catalysis, medicine, and other areas can be expended. The design of hierarchical materials based on native silica material diatomite and MCM-41 has been suggested.

Thus, the unique porous silica materials can be prepared even from inexpensive precursors such as liquid glass or diatomite. The Russian technology for production of granulated moisture-resistant and powdered silica is required and can be elaborated today in cooperation with the Russian academy and industry.

This work was supported by the RFBR Grant (№ 19-43-700008) of the Tomsk Region administration, the state task of the Ministry of Education and Science of Russia (project no. 0721-2020-0037) and Tomsk State University Development Programme (Priority-2030), project№ 2.4.2.22.

Silver-containing binary and ternary oxides: from model objects to catalytic application under ambient conditions

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Current state-of-art in the field of ecology, energy and oil refining causes the problem of searching for and/or developing novel materials with improved catalytic properties in the comparison with systems containing noble metals. Binary and ternary mixed oxides based on silver/copper and transition metals have a great potential for the realization of various catalytic oxidation processes [1–3]. Improvement of reaction properties of mixed oxides are associated with their non-typical crystal structure (paramelaconite, delafossite, crednerite) providing the stabilization of reactive oxygen species [4] and high concentration of defects [5].

This work summarizes the results of investigation of various Ag- and/or Cu-containing mixed oxides ($Ag_2Cu_2O_3$, $AgCuO_2$, $AgNiO_2$, Ag_2CuMnO_4, $AgFeO_2$, $AgMnO_2$) as potential catalysts for low-temperature oxidation reactions including CO oxidation under dry and wet conditions, C_2H_4 epoxidation and selective NH_3 oxidation. Such oxides can be effectively synthesized using co-precipitation or hydrothermal synthesis in alkaline media providing the stabilization of silver in various electronic states in dependence on the preparation conditions and oxide nature: classic Ag^{1+} (in $Ag_2Cu_2O_3$, Ag_2CuMnO_4, $AgFeO_2$ and $AgMnO_2$), deeply oxidized $Ag^{(1+\delta)+}$ (in $AgCuO_2$) or weakly charged $Ag^{(1-\delta)+}$ (in $AgNiO_2$) states. Note that the presence of deeply oxidized metallic states (in the case of $Ag^{(1+\delta)+}Cu^{(3-\delta)+}O_2$ and $AgNi^{3+}O_2$ oxides) was shown to provide the stabilization of highly reactive oxygen species with oxidizing activity at room temperature. However, the regeneration of such species requires the application of additional procedures such as thermo-, photo- or electrochemical activation. In the case of Cu-containing mixed oxides ($Ag_2Cu_2O_3$, Ag_2CuMnO_4) the interaction with reaction media at low temperatures implies the labile surface transitions with participation of copper and manganese (for Ag_2CuMnO_4) species predominantly, while the catalytic properties of other systems ($AgFeO_2$ and $AgMnO_2$) are related to the silver-based transitions between Ag^{1+} and Ag^0 states. In the case of $AgFeO_2$ the irreversible surface modification with the formation of $Ag^0/Ag_{1-\delta}FeO_2$ composite took place, while the pristine surface of $AgMnO_2$ was found to be more stable towards the reaction exposure causing the enhanced catalytic activity at low temperature (even below 0 °C). The realization of various redox transitions on the surface of ternary oxide Ag_2CuMnO_4 is responsible for its improved catalytic activity at room temperature. Moreover, ternary oxide was found to be able to operate effectively for more than 5 h under wet conditions in contrast to traditional hopcalite catalyst. Reaction mixture exposure at temperatures above 300 °C was shown to cause the partial or significant surface modification of studied mixed oxides. Such process was usually accompanied by the release of silver from pristine structure resulting to the formation of Ag^0 nanoparticles.

The layered structure of Ag-based mixed oxides (crednerite or delafossite) as well as labile redox transitions on its surface provides highly effective route of catalytic oxidation at low temperatures (even at $T <$ °C). Synergy between silver and transition metals within the overall structure and chemistry opens up new opportunities for the application of Ag-based mixed oxides as promising catalytic materials.

This work was supported by the Ministry of Higher Education and Science of the Russian Federation, grant MK-503.2021.1.3

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Design and development of new organometallic catalysts for industrial oligomerization and hydrosilylation processes

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The search for new ecologically friendly and resource saving methods and approaches for the preparation of new high effective catalysts for industrial processes of ethylene oligo- and polymerization and hydrosilylation is a key priority in modern synthetic organometallic chemistry [1, 2]. Most important industrial catalysts are based on transition metal complexes and organoelement compounds. Generally, transition metal catalysts require to use co-called co-catalysts, which are represented by highly flammable organoaluminium, organomagnesium or organolithium reagents, capable to activate a pre-form of the used transition metal complex to generate a catalytically active specie. Main chemical role of these activators is to form a potentially catalytically active M-H or M-C bond and create a free coordination site at the metal center for the coordination of the monomer molecule (ethylene, *etc.*).

We have found that the combination of classical chemical synthesis and electrochemical techniques allows to elaborate new methods for selective preparation of organometallic catalysts and generation of catalytically active forms of transition metal complexes avoiding the use of flammable and ecologically dangerous organometallic reagents (MAO, TEA, DEAC TnHA, TiBA, *etc.*) [3, 4]. These methods are of high fundamental and practical interest and can be considered as a new powerful tool for preparation of new and modification of known industrial catalysts operated by worldwide chemical companies like Shell, Chevron Phillips Chemical, DuPont, BP, SABIC, Linde, Axens, *etc.*

Herein we report our recent results obtained in the field of synthetic organometallic chemistry applied towards creation of new methods and new catalysts for industrial application in ethylene oligomerization and hydrosilylation processes. The elaborated methods include the generation and activation of catalytically active organonickel sigma-complexes [4–6], preparation of PCCO-Ni catalysts [7], electrochemical generation of Zr-carboxylate species [8] and organoplatinum complexes with adjustable reactivity in hydrosilylation processes [9–11]. Special attention will be focused on new organonickel catalysts for selective dimerization of ethylene leading to industrially important butene-1 [12].

This work is financially supported by the grant of the President of the Russian Federation for supporting of the Leading Scientific Schools (project no. 4078.2022.1.3) and by the Kazan Federal University Strategic Academic Leadership Program ("PRIORITY-2030").

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Diesel oxidation catalysts PtPd/MnOx-Al_2O_3: effect of Pt/Pd ratio in the catalyst on diesel soot oxidation by O_2 and NO/O_2 in dry and wet feeds

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Together with the diesel exhaust, soot and toxic nitrogen oxides are emitted into the environment. To control diesel emission of carbon monoxide and hydrocarbons, a honeycomb monolithic catalyst with Pt–Pd/MnO_x–Al_2O_3 as a catalytic washcoating was previously proposed [1]. The catalyst had a low total content of noble metals (10–15 g/ft^3 or 0.17–0.35 g/l), but it ensured high oxidation efficiency for CO and CHs due to the thermal activation effect of the Mn–Al–O system [2] as well as the synergistic effect between Pt/Pd and defective Mn_3O_4 particles in catalytic activity [3,4].

The catalyst Pt–Pd(1/2)/MnO_x–Al_2O_3 also showed efficiency in the oxidation of diesel, coal and commercial soot samples with oxygen at temperatures of 400–450 °C [5]. A 300–500 ppm NO in the O_2-contaning feed promoted the rate of soot oxidation (for diesel soot, $E_a = 68 \pm 7$ vs. 100 ± 20 kJ/mol). Due to NO addition, it was possible to diminish the process temperatures to 350–425 °C. A comparison of the kinetic characteristics (rate and activation energy) of the soot oxidation obtained in isothermal and thermoprogrammed modes with properties of the used soot samples has indicated that the reactivity of soot to oxidation depended on the nano- and microstructure of soot as well as on the content of the functional groups on its surface.

In this work, diesel soot oxidation on the surface of the Pt–Pd/MnO_x–Al_2O_3 catalysts, differing in Pt/Pd ratio, and catalyst characteristics (size, morphology and location of Pt/Pd particles) will be discussed in order to reveal the structure – RedOx – activity relationships. Effect of water vapor (5–10 vol.%) in the NO/O_2-containing feeds on the soot oxidation and NO-to-NO_2 oxidation over the catalysts will also be considered.

Activity of Pt–Pd/MnO_x–Al_2O_3 catalysts in soot oxidation was shown to correlate with their ability to NO-to-NO_2 oxidation (in stationary and TPR modes) and with decomposition temperature of NOx-complexes formed on the catalyst surface. The most effective was the bimetallic catalyst Pt–Pd/MnO_x–Al_2O_3 with Pt/Pd weigh ratio equal 2/1 and higher. TPR experiments with NO(1000 ppm)-O_2(2 vol.%)-H_2O (5 %) showed that the catalyst Pt–Pd(2/1)/MnO_x–Al_2O_3 started converting NO-to-NO_2 in wet feed already at 180–195 °C (7–10% of conversion) and reached maximum (48–55%) at 375 °C. Adsorption experiments showed that NOx-complexes was stabilized on the catalyst surface at temperatures of 375 and 425 °C in both wet and dry feeds. It decomposed at 395–420 °C with the release of NO and NO_2.

Water vapor (10 vol.%) promoted the oxidation of soot with both oxygen and O_2-NO-containing feeds, despite the fact that the catalytic conversion of NO-to-NO_2 is inhibited by water vapor. The rate of soot oxidation increased after reaching 25–30% of soot burn-off. According to Raman, DRIFTS, and TPD-Ar data, it is due the removal of amorphous carbon (1500 cm^{-1}), the formation of O-containing groups on the soot surface, and an increase in soot defectiveness (I_D/I_G).

This work was supported by the Ministry of Science and Higher Education of Russian Federation within the government order for BIC (project AAAA-A21-121011390010-7).

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SECTION 1

CATALYST PREPARATION

Synthesis of nanosized and hierarchical molecular sieves SAPO-11 and their application for hydroisomerization of C_{16+} n-paraffins

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Due to the presence of a one-dimensional channel porous structure with a pore size of 4.0×6.5 Å and "moderate" acid sites, catalytic systems based on the SAPO-11 molecular sieve are the most promising for the hydroisomerization of higher C_{7+} paraffins [1], methylation of aromatic hydrocarbons to obtain p-xylene and 2,6-dimethylnaftane [2, 3], gas-phase isomerization of cyclohexanone oxime to caprolactam [4]. At the same time, despite the successful use of SAPO-11 in these catalytic transformations and the creation of industrial catalysts based on it, its microporous structure causes strong diffusion restrictions, which does not allow achieving higher activity, selectivity and stability of catalytic systems based on it [5]. The solution to this problem can be hierarchical and nanoscale molecular sieves SAPO-11, which can significantly reduce diffusion restrictions. The methods proposed in the literature for the synthesis of hierarchical and nanoscale molecular sieves SAPO-11 are based on the use of burnable templates and various crystal growth modifiers. The main disadvantages of such methods are the low degree of crystallinity of the obtained materials and the high cost of templates and growth modifiers, which does not allow the implementation of these approaches on an industrial scale. The aim of this work is to develop a new method for the synthesis of hierarchical and nanoscale SAPO-11 molecular sieves of high phase purity and degree of crystallinity without the use of burnable templates and various crystal growth modifiers.

The paper presents the results on the synthesis of a granular molecular sieve SAPO-11 without binders with a hierarchical porous structure. The method is based on the formation of nanocrystals from a binder in the intercrystalline space of a nanosized seed with the formation of a single splice of SAPO-11 nanocrystals.

The obtained materials were characterized by X-ray phase analysis, ^{27}Al-^{31}P MAS NMR, scanning electron microscopy, low-temperature nitrogen adsorption-desorption, and temperature-programmed ammonia desorption (TPD NH_3).

It has been shown for the first time that the crystallization of granules consisting of seeds (40–70 wt.%) based on nanosized silicoaluminophosphate SAPO-11 (50–200 nm) and silicoaluminophosphate gel-binder composition: $1.0Al_2O_3 \cdot 1.0P_2O_5 \cdot 0.3SiO_2 \cdot 1.0DPA \cdot 10H_2O$ makes it possible to crystallize SAPO-11 in the form intergrowths of nanocrystals (50–200 nm) is an empty space between which forms meso- and macropores. The obtained materials are characterized by specific surface S_{BET}=260–290 m^2/g, micropore volume V_{micro} = 0.08 cm^3/g, mesopore volume V_{meso} = 0.20–0.35 cm^3/g and macropore volume V_{macro} = 0.41–0.50 cm^3/g, total acidity by NH_3 250–550 µmol/g. The synthesized samples were studied in the reaction of hydroisomerization of n-hexadecane and diesel fraction. The high potential of Pt/SAPO-11 with a hierarchical porous structure for the isodewaxing reaction to obtain winter diesel fuel is shown.

This work was supported by Russian Science Foundation № 21-73-00013.

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N-doping of carbon supports of catalysts by NO treatment

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One of the hottest topics of modern research in heterogeneous catalysis is the study of the influence of the catalyst support on the properties of the catalytic system. It has been repeatedly shown that modification of the support may lead to a change in its surface properties as result an increase in the thermal stability of the catalyst as well as an improvement in catalytic activity [1]. One of the ways of such modification is the introduction of nitrogen atoms into the composition of carbon supports using gas treatments. However, it has not yet been established exactly which specific functional groups of nitrogen are responsible for improving catalytic properties and, in addition, some authors believe that functional groups of oxygen can also have a certain effect [2]. Thus, a detailed characterization of modified carbon supports depending on the preparation conditions is necessary for purposeful and controlled modification of catalysts.

In the present study, we prepared a series of Sibunite samples modified in a static Parr-reactor in the presence of NO in gas phase varying treatment conditions (solvent, pre-treatment, gas phase composition, temperature and time of treatment). Qualitative and quantitative analysis of functional groups on the surface of N-doped Sibunites was studied using the X-ray photoelectron spectroscopy (XPS). BET method was used for specific surface area analysis.

It was found that treatment in 15 atm of NO at various temperatures leads to the nitrogen introduction into carbon material. Qualitative analysis of the N1s XPS region shows that, regardless of the processing conditions, we observe following N1s peaks: binding energy (BE) at 399.0 eV and 400.3 eV, corresponding to nitrogen in the carbon matrix, identified as pyridine and pyrrole nitrogen, respectively; BE at 402.9 eV and 406.0 eV assigned to nitrogen in the NOx groups. Analysis of the of the O1s XPS region shows the presence of components, described as C(O)O (531.3 eV), C=O (BE = 532.4 eV), C-OH (533.4 eV) groups and adsorbed water (identification of O1s component from NOx is impeded due to low amount of the state).

The quantitative XPS analysis of surface species shows that processing conditions affect the total nitrogen and oxygen content as well as the ratios of species: the lower the temperature of the NO treatment the higher portion of NOx species. The total N - content reaches the maximum at 180°C, but the highest amount of N of carbon matrix was found for the sample treated at 230°C. The longer the NO treatment, the higher the N of carbon matrix portion.

Obtained data allowed proposing the mechanism of modification of the Sibunite in presence of NO as a process of etching of carbon material layers by the burning on the layer edges. Therefore, at low temperatures, nitrogen is introduced mainly in the form of -NOx groups; but with a temperature increase, the introduction of nitrogen into the carbon matrix is intensifying. The drop of BET specific surface area of modified Sibunites in presence of NO and with increase of NO treatment duration, found in experiments, confirms the assumption about the mechanism of N-doping of carbon material.

The procedure of N - doping of carbon support of the catalysts is developed. Based on XPS study of the samples prepared at different conditions, the mechanism of modification in presence of NO in the gas phase is assumed. Proposed mechanism provides the key to the controlled N-modification of carbon support and catalysts on its base.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation (project AAAA-A21-121011390011-4).

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The catalytic oxidation performance of CO and C_3H_8 oxidation over the MnO_x-ZrO_2-CeO_2 catalysts: the role of the synthesis strategy

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Manganese based oxides are active catalysts in several oxidation and reduction reactions, such as oxidation of CO, VOCs, oxidative coupling of methane, selective reduction of nitrobenzene, CO hydrogenation. Their catalytic properties arise from the ability of manganese to form oxides with wide range of oxidation states and from their oxygen storage capacity in the crystalline lattice. Interaction with cerium/zirconium oxides improves in the catalytic properties due to the formation of "reactive" oxygen species, which are formed both in manganese oxide MnO_x nanoparticles and $Mn_yCe(Zr)_{1-y}O_x$ solid solutions. This work develops two approaches to the formation of active catalysts: 1) synthesis of catalyst by traditional methods of coprecipitation and impregnation; 2) decomposition of solid solutions by the introduction of the topochemical reduction-reoxidation steps.

In the first part, MnO_x-CeO_2-ZrO_2 catalysts were prepared by co-precipitation and impregnation methods have been developed. During preparation, the following parameters were varied: precipitation conditions, calcination temperature, element ratios. The catalysts were studied using a set of physicochemical methods (XRD, XPS, TEM, TPR). A catalytic activity was tested in the oxidation of CO and C_3H_8. For both methods of synthesis, the optimum calcination temperature is 600°C. In the case of impregnation, the highest activity in the oxidation of CO and C_3H_8 is exhibited by the “impregnated” sample based on the support with Zr/(Zr+Ce) = 0.2. Variation of manganese content shows that the optimal value of Mn/(Zr+Ce) is 0.075. In the case of coprecipitation, the Zr/(Zr+Ce) ratio does not significantly affect the catalytic properties. However, with an increase in the manganese content, an increase in activity is observed up to Mn/(Zr+Ce) = 1. A comparison of catalysts with similar chemical compositions, but prepared by impregnation and coprecipitation, showed that the sample prepared by coprecipitation exhibits greater activity. MnO_x-CeO_2-ZrO_2 is characterized by the presence of several active states: 1) relatively large particles of manganese oxides; 2) $Mn_yCe(Zr)_{1-y}O_x$ solid solution; 3) amorphous MnOx particles. Depending on the preparation conditions, different states predominate. Catalysts prepared by impregnation are characterized by the presence of MnO_x and, apparently, a solid solution. In this case, the characteristics of the support determine the catalyst properties. In the case of coprecipitation, $Mn_yCe(Zr)_{1-y}O_x$ solid solutions are predominantly formed on the catalysts.

The second way to prepare an active catalyst includes decomposition of solid solution by the introduction of a topochemical reduction-reoxidation stage. The main idea is that under reducing medium, the surface of the mixed oxide is enriched with cationic Mn^{2+} with further formation of manganese oxide nanoparticles. With further reoxidation, the oxidation of Mn cations is observe leading to the formation of active states of manganese oxides MnO_x. To determine the activation conditions, the temperature of reduction and oxidation, the concentration of the reducing agent, the composition of the mixture during reoxidation, the flow rates, and the treatment mode were varied. As a result, the optimal conditions include the reduction temperature in the range of 350–450 °C, at this temperature, manganese cations already leave the solid solution, but their significant agglomeration does not occur on the oxide surface. For the first time, the processes of exolution of manganese oxides MnO_x are studied in detail by operanso XRD. XPS and TEM methods detect the segregation of manganese cations on the surface of the solid solution. Thus, by adjusting the pretreatment conditions, it is possible to control the phase state and dispersion of the crystalline modifications of manganese oxides, promote the decomposition of the solid solution with the formation of a new type of active states.

This work was supported by the Russian Science Foundation, project 21-73-10218.

Developing block catalysts for ozone decomposition

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Ozone is one of the major pollutants of atmospheric air generated by sunlight photochemical reactions [1]. Such ozone harms agriculture and cities as well as human health: it causes respiratory and cardiovascular diseases. The outdoor ozone pollution leads to indoor pollution. Since most of the time people are indoors, a rapid purification of indoor air from ozone is an urgent task.

Among the existing methods of air purification from ozone (adsorption by activated carbon, thermal decomposition, etc.), catalytic decomposition is a promising approach, since it is characterized by low energy consumption and the absence of secondary pollutants. Supported transition metal oxides attract increasing interest in heterogeneous catalysis, since such catalysts are not inferior in activity to those based on Pt and Pd, and they are significantly less expensive [2]. The use of ceramic blocks makes it possible to integrate such catalysts into air purification systems from ozone, which expands the areas of their practical application.

The aim of this work is to synthesize and study the catalysts based on a composition of transition metals (Mn, Cu, etc.) deposited on a ceramic substrate (cordierite) as well as to study their catalytic properties in the ozone decomposition. Noble metals were not used during the catalyst preparation.

Since the primary support does not possess a developed specific surface area, the synthesis of catalysts was carried out in two stages. The first stage was the preparation of the support, i.e., etching with a weak organic acid to increase the specific surface area of the support. At the second stage, the support was impregnated with a mixture of precursors of active components (transition metal nitrates).

The samples were studied by a complex of physical-chemical methods: low-temperature N_2 adsorption (-196 ºC), powder X-ray diffraction (XRD) analysis, temperature-programmed reduction by H_2 (TPR-H_2), etc. The catalytic characteristics of the samples were studied in ozone decomposition.

According to the low-temperature N_2 adsorption data, the original support features a specific surface area below 1 m^2/g, while the support activation by acid increases the specific surface area up to 99 m^2/g. Further impregnation of the samples leads to a decrease in the specific surface area and pore volume to up to 60–50 m^2/g and 0.015–0.010 cm^3/g, respectively. All samples are characterized by the presence of both micro- and mesopores.

XRD data showed that the support was presented by a cordierite phase, and both activation of support by acid and deposition of active components did not change the sample phase composition. This indicated the formation of weakly crystallized finely dispersed particles of deposited oxides. An increase in the loading of active oxides from 2 to 4 wt.% led to an increase in interfacial interaction between these oxides that was shown by TPR-H_2 data.

The catalytic activity of the synthesized catalysts was studied in ozone decomposition at room temperature and at 50 °C. The ozone conversion was over 90% at a primary ozone concentration of 2.5 ppm.

Thus, the synthesized catalysts based on ceramic blocks and supported transition metal oxides feature a number advantages that make their use for purification of polluted air and ozone decomposition rather promising. Blocks can be made of various shapes, and not only do the developed approaches allow increasing the specific surface of blocks, but also distributing transition metal oxides in a highly dispersed active state on their surface.

The work was carried out within the framework of the state task of the Ministry of Education and Science of Russia (project no. 0721-2020-0037).

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Selective hydrogenation of acetylene over Pd-Co/Sibunit catalysts: The modifying effect of cobalt

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Semi-hydrogenation of alkyne to alkene is widely used to purify crude ethene containing a small amount of acetylene formed during the pyrolysis of petroleum feedstock. However, the depletion of oil reserves will greatly limit the possibility of its use in the future. Thus, the alternative methods for producing ethylene from natural gas or coal through the stage of obtaining acetylene are being intensively developed [1, 2]. In both cases, ethylene is obtained by direct hydrogenation of acetylene on Pd-catalysts modified with Ag, Zn, Ga or other metals [3]. There is evidence that Pd-Co catalysts can also be promising systems for this process due to the possibility of forming bimetallic particles [4]. However, the influence of the active component state of such systems on their properties in the acetylene hydrogenation reaction has not been sufficiently studied. Therefore, the aim of this work was to study the modifying effect of Co on Pd in the Pd-Co/Sibunit catalysts and to establish the relationship between the active component state and catalytic properties in the process of acetylene hydrogenation to ethylene.

Sibunit carbon mesoporous material was used as a catalyst support. Samples were prepared by incipient wetness impregnation method with joint aqueous solution of $Pd(NO_3)_2$ and $Co(NO_3)_2$. The catalysts were dried at 120 °C and reduced in hydrogen at 500–700 °C. The content of palladium in all samples was 0.5 wt.%. The Pd/Co molar ratio was varied from 1/0.5 to 1/2. The state of the active component was studied by XRD, XPS, TEM and EDX. Hydrogenation was carried out in a model gas mixture (4 vol.% C_2H_2 in a hydrogen) in a flow mode at atmospheric pressure at 25–95 °C.

The addition of small amounts of cobalt into the Pd/Sibunit catalyst (Pd/Co = 1/0.5) does not lead to a significant change in the catalytic properties, while an increase the concentration of cobalt to Pd/Co = 1/2 is accompanied by a decrease in catalytic activity and an increase in alkene selectivity. The yield of ethylene on Pd-Co(1:2)/Sibunit is 62%, which is 16 rel.% higher than the yield obtained on the Pd/Sibunit catalyst. According to TEM data, both samples contain spherical particles characterized by an approximately the same size distribution (d_{av} = 4.2 nm). Consequently, the observed differences in catalytic properties are not due to the dispersion value, but due to the difference in the nature of the active component. According to *in situ* XRD analysis, the heating of Pd-Co/Sibunit in H_2 at $T \geq 500$ °C leads to the formation of an fcc phase of the $Pd_{(1-x)}Co_x$ solid solution enriched in Co. An increase in the reduction temperature to 700 °C is accompanied by a gradual increase in the lattice parameter to 3.662 Å, which corresponds to a solid solution containing ~35 at.% of palladium. Pd-Co-catalysts reduced at 600 and 700 °C exhibit lower activity, but the yield of the target product increases significantly to 66 and 68%, respectively. Based on the XPS results, it is assumed that the excellent selectivity of Pd-Co/Sibunit samples is due to a change in the electronic state of palladium under the modifying action of Co. Wherein the decrease in activity can be associated both with the presence of less active bimetallic sites and the partial blocking of the active component by a thin film of cobalt oxide identified by the EDX method.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the governmental order for Boreskov Institute of Catalysis (project AAAA-A21-121011390011-4).

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Synthesis of supported rhodium-containing catalysts on various oxide supports for the catalytic ring opening of cyclohexane

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Decyclization of gasoline and diesel fuel is one of the most important problems of modern oil refining. The presence of cyclic hydrocarbons in the fuel leads to a decrease in its resistance to ignition, as well as to the formation of undesirable products during the combustion of the fuel, for example, the formation of soot in the engine exhaust gases in the case of diesel fuel. One of the possible ways to solve the problem is the hydrogenation of aromatic compounds present in fuels, with the transition of the latter to naphthenes, with the further formation of saturated hydrocarbons. In the case of diesel fuel, decyclization that occurs without skeletal isomerization can also lead to an increase in cetane number, while ring opening of C6–C9 gasoline cyclic components can be useful for increasing the octane number of motor fuels. To consider the decyclization process, cyclohexane is considered as a suitable model compound. The ring-opening reaction of cyclohexane with the formation of n-hexane under certain conditions proceeds on oxide catalysts containing Rh, Ru, or Pt. Interestingly to estimate the influence of the nature and acidity of carriers on the activity of the catalyst and the selectivity for target products. It is assumed that the combination of a sufficiently strong acidic function (zeolites, solid superacids) and electron-deficient metal particles formed during the interaction of an uncharged metal particle with an acid center and the transfer of electron density from the metal to the acid center favors nice for ring opening of cycles. This is often associated with an increased activity of electron-deficient metal particles in the hydrogenolysis of C–C bonds in comparison with uncharged or electron-rich particles, for which high activity in hydrogenation is more typical [1].

The aim of this work is to synthesize a series of catalysts containing 1 wt.% Rh by impregnating supports based on Al_2O_3, SiO_2, $CaO+MgO+Al_2O_3$, $Na_2O+Al_2O_3+SiO_2$ with a solution of $(NH_4)_3[RhCl_6]$; studying of carriers and obtained samples of catalysts by physico-chemical methods of analysis to determine the conditions for the synthesis of catalysts, as well as to determine the qualitative and quantitative composition of the obtained catalysts, carrying out the reduction reaction of cyclohexane on the obtained catalysts and studying the effect of the carrier on the catalytic activity of the catalyst. The synthesis of catalysts included impregnation of carriers with $(NH_4)_3[RhCl_6]$ solution; drying of samples with stirring, calcination in an oven, reduction in a stream of hydrogen at 450 °C.

The catalysts were examined by SEM-EDX, XRD, TGA, TPR-H_2. The prepared samples of rhodium-containing catalysts were investigated in the catalytic reduction reaction of cyclohexane. For each catalyst, the selectivity to n-hexane and the conversion of cyclohexane were determined at temperatures of 275–325°C and a pressure of 40 atm. At the same time, the predominant reaction products with increasing temperature are the cracking products of cyclohexane with composition C1–C5. A high conversion of cyclohexane was achieved when using a catalyst on an Al_2O_3 + CaO + MgO carrier at a temperature of 325 °C – 60.2%. Greater selectivity to n-hexane was achieved using the same catalyst at a temperature of 275 °C – 70.8%.

This work was carried out with a financial support by the Ministry of Science and Higher Education of the Russian Federation (project no. 075-15-2021-591).

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Non-stationary electrolysis in the technology of electro- and catalytically active materials

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The report will discuss the prospects, advantages and limitations of the use of non-stationary electrolysis to obtain electro- and catalytically active materials for various processes of heterogeneous catalysis. The technology of non-stationary electrolysis is based on the phenomenon of dispersion or oxidation/dispersion of electrodes in aqueous electrolytes under the action of alternating pulsed current.

In particular, these are materials based on nanoparticles of platinum group metals as promising catalysts for processes occurring in low-temperature fuel cells [1–3].

Tin oxides, the microstructure and composition of which can be controlled by changing only the anionic composition of the electrolyte and thereby regulating the functional properties of such materials for use in lithium-ion batteries [4], fuel cells [5], and photocatalysis technologies [6].

Graphene-containing materials that find their application as active materials for supercapacitors and lithium-ion batteries [7]. The possibility of non-stationary electrolysis during the simultaneous production of graphene and platinum nanoparticles as an effective anode catalyst for low-temperature fuel cells will be shown [8].

The report will consider both the fundamental foundations for obtaining materials under conditions of non-stationary electrolysis (possible main processes occurring on electrodes under conditions of non-stationary electrolysis and the mechanisms for the formation of the corresponding nanostructures under these conditions will be proposed), as well as technological aspects of obtaining electro- and catalytically active materials under conditions of non-stationary electrolysis.

This work was carried out within the framework of the strategic project "Hydrogen Energy Systems" of the SRSPU (NPI) Development Program during the implementation of the program of strategic academic leadership "Priority-2030".

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Co-based nanofiber-type catalyst for the production of liquid hydrocarbons from synthesis gas

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A complex of the reactions between the carbon monoxide and hydrogen resulting in the formation of hydrocarbon compounds (alkanes, paraffin, olefins, oxygenates) is collectively called Fischer-Tropsch synthesis (FTS). Nowadays, FTS is the most intensively studied process. The researcher's interest is devoted to the development of novel techniques, catalysts, and equipment for the carbon monoxide hydrogenation in order to obtain high yields of the target products [1]. The molecular-weight-distribution of the FTS products depends on the reactor type, process conditions and the nature and structure of the catalyst [2]. Transition metals are the most active for the CO hydrogenation process. The highest catalytic activity can be observed while using Ru, Ni, Co, and Fe. The main problem of FTS catalysts is the active metal stabilization in order to prevent the aggregation and leaching of the active phase. It is known that for the FTS catalysts, weak interaction between the support and active metal is one of the key factors [3].

Metal nanoparticles deposited on polymer matrices are among the most promising materials in catalysis. These composites are characterized by such unique properties as high surface area, high surface energy, and high catalytic activity [4]. Among the methods of synthesis of deposited nanoparticles, in recent years, much attention has been paid to the use of super- and subcritical fluids. The use of water in a sub- or supercritical state in the synthesis of catalysts (the so-called hydrothermal synthesis) makes it possible to obtain highly dispersed particles or ultrathin films of metal oxides from inorganic salts.

In this work, the physicochemical features of the formation of Co-containing catalysts supported on the surface of the polymer matrix of the hyper-crosslinked polystyrene (HPS) were studied using the hydrothermal deposition method. The synthesis of the composite was carried out by the precipitation of metal hydroxides in subcritical water with subsequent conversion of the hydroxide into the oxide phase. The catalytic activity of the samples was studied during the Fischer-Tropsch liquid-phase synthesis using n-dodecane as a solvent.

It was found that the deposition of a metal-containing phase onto a polymer carrier by the hydrothermal method leads to the formation of fiber-type Co_3O_4 crystals with the diameter of 10 nm and a mean length of 500 nm. The study of the catalyst by the method of small-angle X-Ray scattering showed the unimodal distribution of Co-containing particles with the mean size of 10.8 nm. Testing of samples in the Fischer-Tropsch liquid-phase synthesis showed that the catalyst provides over 25 % of CO conversion in a batch mode leading to the formation of over 75% of the yield of liquid C_5-C_{11} hydrocarbons. It was shown that the synthesized composites retain catalytic activity for at least 80 hours in the flow.

This work was supported by the Award of President of the Russian Federation.

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CrO_x/SiO_2 mesoporous catalysts: synthesis using beta-cyclodextrin as a template and catalytic properties in propane dehydrogenation with CO_2

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Propylene is a raw material being produced in a large scale. It is used in the synthesis of cumene, acrylonitrile, acrylic acid, propylene oxide, isopropyl alcohol, polypropylene [1]. Chromium oxide catalysts are widely used in propylene production by propane dehydrogenation. The oxidative propane dehydrogenation is a promising way to enhance this process, but traditional oxidative agents such as O_2 or halogens cause the deep oxidation and thus negatively affect the selectivity to olefins. Thus, the mild oxidative agents are preferable. In the case of using CO_2 as a mild oxidizing agent it is involved in chemical process and so its utilization is attained. The catalytic behavior of the material highly depends on the dispersion of the active phase on the surface of the catalyst. To obtain the high dispersion, the porous carriers are used. Traditionally, the template synthesis is applied to obtain the high-porous materials, such as SiO_2. In this work we used beta-cyclodextrin as a template. Beta-cyclodextrin is a cyclic oligosaccharide comprising seven D-glucopyranoside units linked by 1,4-glycosidic bonds; the molecules have a truncated cone shape. This molecule is interesting because of its ability to form column-like associates in water solutions [2].

This work was aimed at investigation of chromia catalysts obtained with carriers prepared using beta-cyclodextrin and urea as a template and their characterization by different physico-chemical methods to clear the dependencies between synthesis conditions, the structure of the samples and catalytic activity in terms of application of such materials in the oxidative propane dehydrogenation reaction. During the synthesis we varied the used amounts of water as following: $m_{H_2O} = x \times m_{SiO_2}$ where x was 1.5, 5 and 20. The obtained carriers were denoted as SiO_2-1.5, SiO_2-5, SiO_2-20, respectively. The synthetic procedure consisted of tetraethyl orthosilicate hydrolysis with 0.1M HNO_3 water solution, beta-cyclodextrin and urea addition, gelation and gel aging, drying and calcination at 600 °C. This resulted in mesoporous silicas, which were used as carriers. The silicas were wet impregnated with chromium(III) nitrate solution and also dried and calcined at 600 °C under air atmosphere. The amounts of chromium were 3, 5 and 7 wt. %.

The textural properties were investigated by low-temperature nitrogen adsorption-desorption method. All the samples demonstrate large specific surface area (410–680 m^2g^{-1}), while all the pores are mesopores (3–13 nm). Pore size distribution maxima depend on the synthesis conditions: the larger the water amount, the larger pores are formed in the sample while the surface area decreases. Additionally, the silicas were examined by SAXS and the reflexes at about $2\theta = 1°$ took place for the samples SiO_2-1.5 and SiO_2-5. This can be interpreted as a presence of order, but generally the samples are amorphous as can be seen by wide-angle XRD. The catalysts were examined by XRD, XPS, DRS UV-Vis, SEM, TEM, ICP AES, TPR-H_2. All the catalysts were investigated in propane dehydrogenation with CO_2, the selectivity to propylene was up to 80% while propane conversion was 20% on the sample with 7 wt.% on the carrier SiO_2-5. The samples with the carrier SiO_2-5 demonstrate the largest catalytic activity. It can be explained by the combination of optimal porosity, large surface area and also optimal tri- and hexavalent chromium species ratio on the surface. The catalytic results for our catalysts are similar with the performance of the samples using MCM-41 as a carrier, but the difference takes place: our catalysts do not demonstrate the dramatical decreasing of selectivity to propylene while the temperature increases.

This work was supported by Russian Science Foundation, grant no. 20-73-10106.

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MIL-100(Fe)/diatomite composite for photo-Fenton degradation of phenol

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Currently, effective adsorbents and catalysts are used to control environmental pollutions. The highly porous metal-organic framework MIL-100(Fe) can be used as a promising adsorbent due to its high surface area and porosity. It exhibits catalytic and photocatalytic activity due to the presence of Fe ions in the structure. Supporting the MIL-100(Fe) on the surface of a low-cost natural meso-macroporous material diatomite allows creating the material with hierarchical porous structure. The hierarchical porous structure of the composites simplifies the transport of pollutant molecules to MIL-100(Fe) active sites [1].

Composites were prepared by the assembly of the microporous MIL-100(Fe) in the meso-macroporous structure of diatomite ("Kvant" company, Russia). A "composite_«one pot»" sample was obtained by hydrothermal single-stage method. The iron (III) nitrate solution (5.3 g in 11 ml H_2O) and trimesic acid were added to 10 g of diatomite, the mixture was kept in a steel autoclave at 160°C for 12 h. To obtain a composite_impr sample, 10 g of diatomite was impregnated by iron (III) nitrate solution (5.3 g) by moisture capacity and dried at 120°C for 4 h. Then, the trimesic acid solution was added, and the mixture was kept in a steel autoclave at 160°C for 12 h. The synthesized samples were washed with water and ethanol, then were dried at 120°C for 4 h.

The porous structure of the samples was studied by low-temperature N_2 adsorption on the 3Flex specific surface area and porosity analyzer (Micromeritics, USA). To measure the sorption capacity towards toluene vapor, the degassed samples were placed in a desiccator with a saturated toluene vapor and kept until the samples were saturated with the toluene vapor. Catalytic activity of the samples was studied in a model reaction of phenol oxidation in an aqueous solution with hydrogen peroxide at room temperature and atmosphere pressure under vis-irradiation [2, 3]. The concentration changing was recorded by the spectrofluorimeter Solar CM2203 (SOLAR, Belarus).

The N_2 adsorption-desorption isotherm for the obtained samples indicates the presence of micropores in MIL-100(Fe) and mesopores in diatomite. Thus, this indicates the hierarchical porous structure of the composites: the presence of wide pores larger than 50 nm and pores of 0.6–4 nm in size. The obtained MIL-100(Fe)/diatomite composites are characterized by a relatively high surface area (441 m^2/g and 322 m^2/g for composite_«one_pot» and composite_impr, respectively). In addition, they possess high sorption capacity of toluene ($a = 254$ and 160 mg/g, respectively) that is higher than for some common microporous and mesoporous sorbents [4]. The complete phenol decomposition occurs in the presence of MIL-100(Fe) and the composite_«one_pot» sample in 100 and 80 min, respectively. Kinetic curves are straightened in 1st order coordinates. Reaction constants for MIL-100(Fe) and composite_«one_pot» are 0.051 and 0.065 min^{-1}, respectively.

Thus, MIL-100(Fe)/diatomite composites with the hierarchical porous structure (micro-meso- and macropores) were obtained by a hydrothermal synthesis. The materials showed a relatively high sorption capacity of toluene vapors and catalytic activity in phenol photodegradation.

This work was supported by the RFBR and Tomsk region (project No 19-43-700008).

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Mixed oxides $AgFeO_2$ and $AgMnO_2$ as novel catalytic materials for low-temperature CO oxidation

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Mixed oxides containing catalytically active transition metals are promising objects in the field of oxidative catalysis. Layered structure of mixed oxides is usually characterized by the presence of defects such as stacking faults and vacancies providing a significant activity in the processes of catalytic oxidation. Therefore, silver-containing oxides with layered structure have a great potential for catalytic application at low temperature, for example, in catalytic CO oxidation [1] as industrially and ecologically important process. Widely used methods for the synthesis of mixed oxides with layered structure include co-precipitation, hydrothermal synthesis and high-temperature solid-state reaction. But only co-precipitation and hydrothermal synthesis can be applied for the preparation of catalytic materials with developed surface area and appropriate textural characteristics and porous structure.

This work is devoted to the preparation and catalytic characterization of silver-containing layered mixed oxides $AgMnO_2$ and $AgFeO_2$ with crednerite and delafossite structure, respectively. Such oxides were obtained using co-precipitation or hydrothermal synthesis. The preparation conditions were optimized to achieve the improved catalytic properties of mixed oxides in the CO oxidation reaction. To study the evolution of the surface state and surface composition as a result of treatment with various reaction media (CO, O_2 or CO+O_2) the *ex situ* XPS technique was applied. Structural features and phase transformations were investigated using *in situ* X–ray diffraction.

It was found that relatively low temperature of $AgFeO_2$ synthesis (≤120 °C) provides delafossite phase with high dispersion (20-40 m^2/g) and developed defect structure. The structure of the most catalytically active samples was characterized by the presence of high concentration of stacking faults (microtwinning) providing an evident catalytic activity in CO oxidation already at room temperature: CO conversion at 25 °C was near ~5%, while CO conversion close to 50% was achieved at 70–100 °C.

It was shown that a decrease in the amount of oxidizing agent ($Na_2S_2O_8$) used during the synthesis of $AgMnO_2$ leads to the preparation of amorphous product, while the following calcination at 450 °C resulted in the crystallization of crednerite structure without any other crystallized phases. The most active sample of $AgMnO_2$ was obtained using KOH as alkali media, whereas the NaOH media leads to contamination of the surface of $AgMnO_2$ with sodium. Remaining sodium on the surface was shown to be responsible for a decrease in low-temperature catalytic activity. The synthesis using KOH provided the enhanced catalytic activity of $AgMnO_2$ operated effectively even below 0 °C and CO conversion close to 50% was achieved at room temperature.

Based on all obtained data including the results of *ex situ* XPS and *in situ* XRD, we supposed about different structure of active surface of layered oxides $AgFeO_2$ and $AgMnO_2$ under CO+O_2 reaction conditions. In the case of $AgFeO_2$, the irreversible release of silver from the delafossite structure with the formation of the $Ag^0/Ag_{1-x}FeO_2$ composite takes place. It indicates that such composite determines the catalytic properties of $AgFeO_2$ particles with delafossite structure. At the same time, for $AgMnO_2$ there are attributes of preservation or minimal modification of the original crednerite structure with a possibility for reversible transition between $Ag^0/Ag_{1-x}MnO_2$ composite and $AgMnO_2$ oxide. In this case, it is assumed that the initial surface of the $AgMnO_2$ crednerite is responsible for enhanced catalytic activity in CO oxidation.

This work was supported by the Russian Science Foundation, grant #21-73-00183.

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Ag/SiO_2 monoliths in the continuous-flow liquid-phase hydrogenation of p-nitrophenol

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Hierarchical porous monoliths have a high porosity and a large surface to volume ratio. This makes it attractive for use as a catalyst support in flow reactors. The flow reactor has advantages that allow reactions to be carried out more selectively and safely due to efficient mixing, improved heat and mass transfer [1]. Silica monolith consists of a porous skeleton with mesopores and interskeletal macropores. Due to the widely studied silica surface chemistry, the structure and composition of the catalyst can be controlled during the synthesis. The size and shape of the catalyst depends on the container in which it is prepared [2]. Recent studies [3] showed the successful implementation of monolithic catalysts in various chemical and biochemical flow processes. However, in order to use the full potential of the porous silica monoliths as flow reactors, several problems still need to be solved. For example, the effect of structure on the properties and catalytic activity of monolithic catalysts, as well as their role in diffusion limitations, has been little studied. The aqueous-phase hydrogenation of p-nitrophenol to p-aminophenol with excess NaBH4 as a reducing agent was used as a test reaction to study the influence of structure of the silica monolith on catalytic activity in continuous flow. In addition, nitrophenol is a wastewater pollutant and can adversely affect humans and the environment. The 4-aminophenol formed during the reduction process is used in the pharmaceutical industry, the production of paints, etc.

Here, we report the study of catalytic activity of cylindrically shaped Ag-loaded silica monoliths. For the preparation of catalysts, silica monoliths with two mean macropore width of 7 or 21 μm and mesopore width of 5–50 nm or 5–38 nm were obtained, which were designated A65 and A60, respectively. The monolithic catalysts were prepared by reducing silver nanoparticles in the pores of the support.

It was found that silver particles are distributed on the surface of the skeleton and in mesopores. Moreover, the catalyst Ag/A65 with a smaller macropore size is characterized by a narrower distribution of the silver particles over the surface of the skeleton. Catalysts were placed in heat shrink tube for use as a flow reactor. No influence of flow rate on conversion at a fixed contact time was observed. This indicates the absence of external mass-transfer limitations or stagnant layer formation in the macropores of the monolithic catalysts. The effective rate constants of the hydrogenation of 4-nitrophenol were determined. For the Ag/A60 catalyst, the effective reaction rate constant was lower than for Ag/A65. This is probably due to the effect of internal diffusion on the rate of the catalytic flow reaction in the Ag/A60 catalyst with the narrower mesopore size distribution.

Thus, for the synthesis and successful application of catalysts based on monolithic porous silica in a flow reactor, it is necessary to find a balance between its structure (high permeability, low pressure drops, strength, mesoporous structure) and the distribution of the active component in the catalyst.

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The impact of Nb_2O_5 in the composition of MoS/γ-Al_2O_3 catalysts to the morphology of the active phase particles

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One of the ways to improve the efficiency of hydrotreating catalysts is to introduce inorganic modifiers into their composition [1] A wide variety of compounds have been proposed as modifying additives. The optimal content of such additives in the catalysts is usually determined empirically. The mechanism of action of modifiers is also not always clear and is the subject of research. From this point of view, Nb-containing compounds are of practical interest, since, according to the literature, their use in catalysis can be carried out as an active component, modifier, or support [2].

The aim of the study was the synthesis of NbMo catalysts, the investigation of the composition, physical chemical characteristics and catalytic properties of sulfide Mo/γ-Al_2O_3 catalysts modified by Nb.

A series of NbMo/γ-Al_2O_3 catalysts and a Mo/γ-Al_2O_3 reference one were prepared in this work. The content of active metals on the catalysts was constant and equal to 10 wt.%, however, the molar ratio of Mo to Nb changed (the molar ratio of Mo to Nb in 4 samples was 1:0, 11:1, 3:1, 1:1).

The catalysts were synthesized by wetness impregnation with a solution of phosphomolybdic acid and niobium oxalate, followed by drying at 120°C. Catalysts were sulfided in gas phase at 400°C and 1 MPa in an H_2S/H_2 atmosphere (10/90 vol.%) for 2.5 h.

Sulfided NbMo/γ-Al_2O_3 catalysts were characterized by HRTEM in order to acquire more information about the effect of the incorporation of Nb on the morphology of the active phase. Statistical analysis of the active phase particles slab length, stacked layer number, and the ratio of edge to corner active sites was carried out for the samples. Morphological characteristics of the MoS_2 active phase of the catalysts were statistically evaluated from more than 300 crystallites of MoS_2 observed in several HR TEM images. The active phase dispersion on the catalysts surface was obtained as f(Mo) and is equal to the number of surface Mo atoms divided to the total number of Mo atoms, calculated for average MoS_2 particle.

It was found that Nb incorporation to the Mo-catalysts improved the morphology of MoS_2 active phase. Both average slab length and average stacking number of MoS_2 crystallites were smaller in the Nb-modified catalysts. With an increase in the amount of Nb in the composition of the catalysts, the average length decreases from 4.2 to 3.3 mn. The average stacking number decrease from 2.0 to 1.6.

The average slab length was used to determine the dispertion of Mo atoms located on the edge surface of MoS_2 particles, assuming that the MoS_2 crystallites are perfect hexagons [3]. This value can be considered an indicator of the amount of catalytically active Mo species. It was shown that, with an increase of the Nb content in the catalysts, f(Mo) value increases from 0.28 to 0.35. It is also interesting that the ratio of edge to corner active sites decreases at the same time.

Thus, according to the HR TEM investigation of NbMo/γ-Al_2O_3 catalysts, the introduction of Nb improves the morphological characteristics of sulfide active phase particles of the NbMo-catalysts. Samples of catalysts with improved morphology showed increased catalytic activity in hydrotreating reactions.

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Preparation of the Pt-Sn-In/Al_2O_3 system as reforming catalyst

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Alumina-platinum catalysts have been one of the most common catalytic systems for many decades and are widely used in oil refining, petrochemistry, and gas emission neutralization processes. This system most clearly demonstrated its efficiency in the process of catalytic reforming [1]. Modern reforming catalysts are complex systems that include various modifiers – Re, Sn, Ir, In, which contribute to an increase in the dispersion of Pt particles and increase the stability and selectivity of the catalytic system.

In-containing systems are of interest for obtaining an increased yield of high-octane reformate. There are data indicating an increased selectivity of the isomerization of hydrocarbons of the C_{5+} series for such systems [2, 3].

For catalysts preparation spherical industrial γ-alumina was used as a carrier (two carriers were studied in this work, containing 0.2 wt.%. Sn and without modifiers). 0.2 wt.% In was applied by vacuum impregnation of the carrier from indium nitrate aqueous solution. The deposition of chlorine and platinum was carried out from solutions of acids in excess water in the amount necessary to obtain 0.25 wt.% Pt and 1 wt.% Cl^- on the catalyst. The catalysts were calcined in an air stream at 500°C for 1 h and reduced in a hydrogen atmosphere at 500°C for 1 h.

The dispersity of platinum atoms in the prepared catalysts was determined by CO chemisorption. It is shown that the addition of In reduces the size of Pt atoms compared to the initial sample, but to a lesser extent than Sn. In trimetallic systems, the dispersion of Pt has intermediate values.

The process of heptane reforming (study of catalyst activity) was carried out under the following conditions: 0.44 MPa pressure, 460, 480, 500°C temperatures, LHSV = 3 h^{-1}, hydrogen/feedstock ratio = 3:1 (mol.). Stability tests were carried out under similar conditions at a temperature of 500°C for 3 hours, the sampling of reforming products was carried out every 30 minutes.

Based on the results of catalytic tests of the samples heptane conversion, selectivity for isomers, and also selectivity for aromatic hydrocarbons were calculated.

According to catalytic tests, the introduction of 0.2 wt.% In to the Pt/Al_2O_3 inhibits the yield of aromatic hydrocarbons. However, the addition of In as a third metal to the bimetallic Pt-Sn system makes it possible to obtain a reformate with a higher octane number and increase the yield of a stable reformate. This behavior of the catalyst is directly related to a more optimal combination of acid sites of different strengths, which are responsible for accelerating reactions of a certain type.

The acid-base properties of the catalysts were studied by IR spectroscopy of CO adsorption, and their connection with the catalytic properties of the systems under study was shown.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the governmental order for Boreskov Institute of Catalysis (project AAAA-A21-121011890074-4).

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Technology development for a domestic production of high purity alumina

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Alumina is among the widely used catalyst supports due to its high specific surface area (up to 500 m^2g^{-1}) [1], developed porosity, amphoteric property of the surface (acidic or basic), high concentration of surface active sites, and a wide range of crystalline phases available for this material. Aluminum hydroxides of various forms and stoichiometry are the basic reagents for the production of alumina, with the properties of the latter directly linked to those of the former.

With a specific focus on the catalytic applications, one should mention high purity aluminas, that are crucial to such fields as HC reforming, dehydrogenation, hydrotreating, and others. One of the key methods for the production of the high-purity alumina supports is alkoxide technology [2], as practiced by, for example, Sasol (a leading supplier). Presently, a domestic industrial production of high-purity alumina by either technology is not realized – a challenge that requires an ever more urgent response. In light of this, an approach using readily available technical grade aluminium hydroxide (gibbsite) is of interest. The process involves two reactions, firstly, gibbsite is dissolved in nitric acid, followed by a precipitation of pseudo-boehmite by ammonia. The by-product of the process, therefore is ammonium saltpeter – a valuable chemical for various applications (agriculture, mining, *etc.*). Although this approach is known in the field, the detailed knowledge, both in terms of the fundamental background and application, is largely missing.

The aim of this project is to develop synthetic approaches of the high-purity alumina carriers with controlled architecture using nitric acid-ammonia re-precipitation method. This goal is being achieved via two routes, firstly, we want to establish a fundamental understanding of the levers controlling key product properties (purity, SSA, porosity, *etc.*). Secondly, based on this knowledge we will work to provide a mature technology solution (TRL 5 and higher) within an academia-industry partnership framework. The general approach realized in this project, therefore, combines fundamental knowledge creation with an eye towards a technological feasibility.

Present report details the bench-scale results of the synthesis of aluminum hydroxides via a nitric acid-ammonia re-precipitation from a technical grade gibbsite provided by one of the large-scale domestic manufacturers. The examination of the impact of various process parameters (temperature, stage duration, pH, precipitate aging conditions), revealed the main dependencies and process optimization opportunities with an aim of producing quality product, as characterized by XRF, XRD, ICP-OES, BET, TGA. Specifically, the use of an XRD allowed us to identify necessary washing conditions of the precipitate minimizing waste fluid accumulation, while generating pure pseudo-boehmite phase. BET data suggests an existence of an optimum aging time of the precipitate featuring the highest SSA. Precipitation stage pH was found to play a role in the formation of product porosity, allowing one to fine-tune this parameter depending on the application. This work also involved the development of a robust analytical methodology for alumina determination, that can find its use in a high paced industrial setting. Finally, we present the results of a synchrotron XRD study that allowed us to gain detailed insights into the phase transition dynamics within the precipitated product.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the governmental order for Boreskov Institute of Catalysis (project AAAA-A21-121011390007-7).

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One-step synthesis of highly porous aromatic polymers – supports for Pd catalysts of Suzuki cross-coupling

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Palladium catalysts are one of the most important and interesting objects for research due to their wide range of applications in fine organic synthesis and, in particular, in cross-coupling reactions [1].

Hyper-cross-linked polymers are prospective catalytic supports. These polymers have advantages such as diverse synthetic methods, easy functionalization, high surface area, and low cost. Thorough selection of monomers, cross-linkers and optimized reaction conditions allows obtaining polymer with an adjusted porous topology. To date, numerous hyper-cross-linked polymers have been prepared by post-cross-linking of polystyrene-based precursors, one-step self-polycondensation or external cross-linking strategies. The development of these methods made possible synthesis of well-defined porous polymer networks with customized micromorphology and functionalities [2].

In this work, a series of highly porous aromatic polymeric supports and palladium-containing catalysts based on them was synthesized by the one-step cross-linking method. Polymers were synthesized at variation of the type of monomers and their ratio. Synthesis of aromatic polymers was based on the use of methylal as cross-linking agent in the presence of anhydrous $FeCl_3$ as a polymerization catalyst. This approach allows applying various monomers, for example, substituted arenes and heterocyclic aromatic compounds. In this work, benzene, naphthalene, anthracene and also different combinations of them were used as monomers. As a result, a series of polymers having specific surface area more than 900 m^2/g were synthesized and used as supports for palladium.

Pd-containing polymeric catalysts (1-1.5 wt.% of Pd) were tested in a model reaction of Suzuki cross-coupling between 4-bromoanisole (1.0 mmol) and phenylboronic acid (1.5 mmol) in the presence of NaOH (2.0 mmol) at 60 °C using ethanol-H_2O mixture (5:1) as a solvent. It was shown that the use of synthesized polymeric catalysts allows achieving more than 95% of 4-bromoanisole conversion in 1 h of the reaction with high selectivity with respect to cross-coupling product – 4-methoxybiphenyl.

This work was supported by the Russian Science Foundation, grant number 20-19-00386.

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Synthesis of LSX zeolites and their N_2 adsorption behavior

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Zeolites belong to a class of inorganic crystalline materials widely used in sorption, catalysis, liquid drying, gas separation and purification. At present, there is a significant demand for high-purity oxygen used in various fields. One of the ways to produce pure oxygen from an air gas mixture is adsorption separation on low-modulus zeolites of the LSX type (low-silica X).

Not only do the separation of air and production of pure O_2 over LSX zeolites occur due to the molecular sieve effect but also due to the ion–quadrupole interaction of extraframework cations (Li^+, Ca^{2+}, Ag^+) with nitrogen and oxygen molecules of similar size. The LiLSX zeolites were established to possess high nitrogen sorption capacity; they can be used to produce oxygen with a purity of up to 96%. Partial ion exchange of Li^+ for Ag^+ can enhance nitrogen adsorption at low pressures (up to 30 kPa) that is important when using zeolites in PSA (pressure swing adsorption).

The aim of this work was to establish the effect of silver loading in AgLiLSX zeolites on room-temperature nitrogen adsorption.

Two series of LSX zeolites with different S_{BET} (434 and 650 m^2/g) were prepared. The initial KNaLSX zeolite was synthesized by the sol-gel method followed by crystallization of amorphous alumina-silica gel at 50°C for 72 h. Then, K^+ and Na^+ ions were ion exchanged by Li^+ and then by Ag^+ ions. Zeolites were studied by XRD, low-temperature N_2 adsorption, UV spectroscopy, atomic emission spectroscopy, and nitrogen adsorption at 25°C.

The formation of zeolites with the LSX structure was confirmed by XRD, all zeolite samples featured a high degree of crystallinity. According to the low-temperature N_2 adsorption-desorption data, it was revealed that all the synthesized samples were microporous. According to the Howarth-Cavazoe method, differential pore size distribution curves indicated that all samples of both series were characterized by micropores of 0.54–0.57 nm in size.

Nitrogen adsorption at room temperature showed that the initial form of the KNaLSX featured a low nitrogen adsorption (3.0–4.5 cm^3/g). The LiLSX samples had the highest adsorption capacity to nitrogen, and the maximum adsorption value was determined by the content of Li^+ (above 15 cm^3/g). At low pressures (up to 30 kPa), the AgLiLSX zeolite with the maximum silver content (the maximum degree of exchange of lithium by silver) had the highest N_2 adsorption and characterized by a larger specific surface area than the AgLiLSX of another series.

Thus, the amount of extraframework cations – nitrogen adsorption sites – is determined by S_{BET}; the adsorption properties of the AgLiLSX are affected by the degree of substitution of Li^+ by Ag^+. It has been established that the presence of Li^+ is required for effective nitrogen adsorption on the LSX-type zeolites, and an increase in the silver loading leads to an increase in N_2 adsorption in the low-pressure region.

The study was supported by the Tomsk State University Development Programme (Priority-2030), project№ 2.4.2.22.

In situ growth of palladium nanoparticles inside the microfluidic chip monitored by X-ray absorption spectroscopy

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Bimetallic nanoparticles find various applications in different fields including catalysts. In particular, catalysts based on gold and palladium are promising materials for the conversion of methane to methanol, which is of great economic importance. Several studies suggest that photostimulation of bimetallic catalysts in this reaction will improve this technology, which will significantly reduce the cost of the reaction and increase the economic feasibility of this process. Rational optimization of the nanoparticle structure and properties by varying the parameters of a synthetic procedure is therefore an important fundamental and practical problem.

XRD, UV-Vis, TEM, XPS, SEM and XAS are one of the most often used analytical techniques to characterize the structure of bimetallic nanoparticles. For Pd and AuPd nanoparticles, that do not possess the strong plasmon resonance as pure gold particles, X-ray based techniques, such as X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD) can be advantageous over optical ones. However, small sample quantities, low concentration of the nanoparticles and difficulties to apply in the in situ regime, are preventing from using them for online optimization of the synthesis parameters.

We have developed a microfluidic device for in situ synchrotron-based synthesis of nanoparticles, which was successfully tested by monitoring the growth of palladium nanoparticles in toluene from Pd(II) acetate precursor by in situ XAS. The microfluidic device was printed on Ultimaker 3d printer, the material of the chip was PETG. The dimensions of the chip are 97x85x5 mm with two inlets and one outlet. The microchip is divided into the mixer zone with the total volume of 0.75 ml and the reaction zone with 10 microchannels with the length of 80 mm and the cross section of 1.5x1.5 mm^2. An X-ray beam was aligned on each channel. The optimized length of the microchannels allowed for high-quality data collection in both XANES and EXAFS regions even for low concentration of metal in the solution and to convert the space-resolved data into time evolution of Pd(II) -> Pd(0) conversion. To the best of our knowledge this is the first case of in situ XAS study of the growth of palladium nanoparticles inside the microchip, and the first experimental report of aligning the beam not perpendicular but parallel to the channels, which opens new possibilities for online control and optimization of the synthesis parameters.

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Application of sorption methods of analysis for the development of catalysts based on noble metals

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Noble metal catalysts are widely used in the hydrogenation/dehydrogenation of liquid organic hydrogen carriers (LOHC) [1].

The vast majority of heterogeneous petrochemical catalysts consist of an active component and a carrier. Various porous materials used as carriers, such as aluminum and silicon oxides, aluminosilicates and zeolites. The role of the active phase in hydrogenation/dehydrogenation catalysts predominantly played by noble metals (Pt, Pd, Re, Rh) in various compositions [2]. Both the properties of the support and the properties of the active phase have a direct impact on the final activity and selectivity of the catalysts. When developing catalysts, researchers follow the path of primary evaluation of catalytic activity, which takes a rather long time. An alternative direction can be the use of a complex express method for the analysis of the physicochemical properties of catalysts.

The relevance of this study lies in the development of a complex express method (thermogrammed reduction, pulsed chemisorption) for the development of catalysts based on noble metals. This approach will make it possible to obtain detailed physicochemical and catalytic properties, which, in the future, will make it possible to carry out a primary selection of catalysts without long-term catalytic tests. This development will significantly reduce the time spent on the development of catalytic systems, as well as reduce operating and labor costs in laboratories and plants for the production of catalysts.

In this work, we have developed a comprehensive analytical procedure for the evaluation of noble metal catalysts for the TPDRO1100 instrument. For catalysts, such parameters as dispersion, number of active sites, average particle size of the active phase were determined, and the propensity of the active phase to be reduced was also analyzed. The catalytic properties of the catalysts studied in the reactions of hydrogenation of biphenyl and dehydrogenation of bicyclohexyl under the conditions of a flow unit. The influence between the amount of absorbed adsorbate gas and their activity in these processes has been established.

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Microwave-assisted synthesis of Ni-Co on carbon catalysts for the Mizoroki-Heck reaction

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Application of the transition metals (Ni, Co, Cu etc.) on a carbon matrix instead palladium and its derivates as a catalyst can reduce the cost of production based on cross-coupling reactions [1,2]. Microwave-assisted decomposition of the thermally unstable metal salts deposited on graphite is one of the preparation methods for metal on carbon (M/C) catalyst [3]. The advantages of this method are relative simplicity and the absence of the chemically metal reduction necessity. This method also opens the opportunity to form nanoparticles of the several metals solid solution, which can be an instrument of the catalytic activity increase.

In this work, a graphite-based catalyst decorated with Ni-Co nanoparticles was obtained. Ni and Co were taken in the ratio of 1:2 [4]. Ground graphite powder (0.25 mol) was added to a solution of $Ni(NO_3)_2 \cdot 6H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ (2.5 and 1.25 mmol), sonicated, and dried until completely evaporation of water. The mixture was heated via microwave radiation in the air and cooled in the rarefied atmosphere created by a water jet pump. Heating was carried out in an air atmosphere. XRD analysis of the resulted composite shown that metals were represented by the Ni-Co solid solution nanoparticles with an average size of 70–100 nm.

The resulting catalyst was tested in the cross-coupling reaction of Mizoroki-Heka 1-iodine-4-nitrobenzene (3.5 mmol) and styrene (5.25 mmol). Dimethylformamide and triethylamine were used as a solvent and base. The mass of the catalyst corresponded to ≈0.3 mmol of pure metals. The reaction was carried out at a temperature of 130 °C in 3 stages of 4–5 hours. After the first stage, the catalytic activity disappeared. The resulting mixture of products was dissolved in acetonitrile for subsequent spectrophotometry. The yield of 4-nitrostilbene was measured UV-VIS spectrophotometrically. The conversion of 1-iodine-4-nitrobenzene in 5 hours was 20%.

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Catalytic properties of the product of autoclave thermolysis of a platinum and non-ferrous metal ammoniates mixture

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Supported catalysts are widely used in various industrial processes. These are complex systems consisting of an inert support, carrier, main catalytic component, and promoter additives. The chemical composition of the components and the geometry of the carrier and catalytic centers, which depend on the choice of the precursor compound and the method of its transformation into the catalytically active phase, determine the operational properties of such a system. Many studies have shown the relevance of using binary complex compounds as precursor compounds [1–2].

The autoclave thermolysis of platinum and non-ferrous metals complexes is a promising method for obtaining supported catalytic phases [3–6]. It makes it possible to combine the formation of a catalytic phase and its deposition on a support. The method allows the use of supports such as metals and their alloys, which have a number of advantages over oxide supports.

The aim of this work was to obtain and study mixed metal oxide catalysts supported on a metal carrier from of a mixture solutions of platinum and non-ferrous metals ammonia complexes under autoclave conditions.

Ammonia complexes of platinum $[Pt(NH_3)_4]Cl_2$ or palladium $[Pd(NH_3)_4]Cl_2$ and nonferrous nickel $[Ni(NH_3)_6]Cl_2$ or cobalt $[Co(NH_3)_5Cl]Cl_2$ complexes were used as precursor compounds. The facing of stainless steel served as the carrier. A carrier, a solution of precursor compounds, and 0.01M KOH until pH 8-9 were placed in a fluoroplastic insert. The solution was deaerated, then pressurized in a metal autoclave and heated to 190°C for 150 min with constant stirring.

We studied powdered products of autoclave thermolysis of two ammoniates using the methods of scanning electron microscopy, energy-dispersive X-ray microanalysis and optical emission spectrometry with inductively coupled plasma.

The thermolysis product of a mixture of complex compounds is a fine black powder, consisting of mixed cobalt oxide or nickel hydroxide, on which precious metal particles are reduced.

We tested the obtained catalysts in the reaction of the complete oxidation of propane and n-hexane in a flow unit with analysis of the reaction mixture by gas chromatography. The activity of the multicomponent catalyst was compared with the activity of a monometallic platinum catalyst obtained under similar conditions on the same metal support. The tests performed have shown that multicomponent catalysts exhibit high catalytic activity in the oxidation of hydrocarbons. The Pt/Co_3O_4 catalyst exhibits an activity comparable to that of Pt on stainless steel facing at temperatures above 300°C. A comparison of the results of samples deposited on stainless steel facing from different precursor compounds showed that the catalytic phases deposited from platinum and cobalt ammonates at 250–300°C exhibit higher activity than those obtained by decomposition of the binary complex $[Co(NH_3)_5Cl][PtCl_4]$.

Thus, the use of autoclave technology and complex precursor compounds can form the basis of a promising method for the preparation of heterogeneous catalysts.

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Synthesis of micro-mesoporous ZSM-5 from natural halloysite nanotubes and its application for hydroisomerization of C-8 aromatic fraction

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Zeolite ZSM-5 is one of the most common components of heterogeneous catalysts, which are widely used in many petrochemical processes, such as cracking, isomerization, aromatization and alkylation.

The classical hydrothermal synthesis of zeolite ZSM-5 has been well studied and consists in the preparation of an aluminosilicate gel with the addition of an organic template. Among the many structure-directing agents that are used in the synthesis of zeolite ZSM-5, TPABr is considered the most effective. However, there are obvious disadvantages of synthesis using an organic template, such as the high cost of production, pollution of wastewater and air because of its thermal decomposition. Therefore, a lot of work is currently underway aimed at developing an efficient, cost-effective and environmentally friendly method of producing zeolite ZSM-5.

Another of the modern directions for modifying the synthesis of ZSM-5 is the use of inexpensive natural aluminosilicate materials as precursors of silicon and aluminum oxides: rice husk ash, kaolin, rectorite, perlite, diatomite and paligorskite. These minerals are more accessible and cheaper than chemical reagents, and thus the synthesis of zeolite ZSM-5 using them can significantly reduce the cost of its production.

In this work, zeolite ZSM-5 was synthesized by template and template-free methods using halloysite nanotubes as silica and alumina sources. The functional materials were molded using boehmite as the binder. In order to obtain Pt-catalysts, the supports were impregnated with a $H_2PtCl_6{\cdot}6H_2O$ solution, the calculated Pt content was 0.5 wt.%.

At each synthesis stage, the materials have been characterized by a complex of physico-chemical methods of analysis. The catalysts were tested in isomerization of an industrial C-8 aromatic cut in a fixed-bed flow reactor under the following operating conditions: temperature range – 360–420 ºC, hydrogen pressure – 1.0 MPa, liquid hourly space velocity (LHSV) – 4–6 h^{-1}, H_2/feedstock volume ratio – 1200 $L_{n.c.}\ L^{-1}$.

Both catalysts demonstrate high activity. With their use, it was possible to reach 100% conversion of ethylbenzene. In the presence of a catalyst obtained by the template method, trimethylbenzene isomers are formed, from which it can be concluded that it promotes the isomerization process in parallel along two routes – mono- and bimolecular [1,2]. A catalyst synthesized without the use of a template initiates reactions proceeding along a monomolecular route largely, which leads to a decrease in the number of side reactions (disproportionation, transalkylation and dealkylation). The ratio of para-/ortho-xylenes in the resulting product practically does not change with increasing temperature and LHSV. The maximum value (1.09) is achieved on a template-free catalyst at 360 ºC and LHSV = 6 h^{-1}.

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Influence of the Co/Cu ratio on the formation of active centers of CoCuAl-catalysts based on layered double hydroxides for the selective hydrogenation of furfural

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Catalytic hydrogenation of furfural is an important industrial process that can be used to obtain valuable chemical compounds (high-octane fuel additives, solvents and components of antifreezes). At present, the development of nontoxic, active and selective catalysts for this reaction is an urgent task. Promising systems are cobalt-containing catalysts due to their high activity, low cost and high selectivity for the formation of furfuryl alcohol. The introduction of copper as a second metal into the composition of such a catalyst can contribute to a finer control of the selectivity of the catalysts due to the possible interaction between the hydrogenating metals. In this work, we used a special approach consisted in the introduction of hydrogenating metals into the composition of layered double hydroxides (LDH) at the stage of their synthesis. We expected this approach to provide a uniform distribution of metals at the atomic level, which will contribute to their high dispersion in the catalyst.

The aim of this work was to synthesize catalysts based on CoCuAl-LDH and to study the effect of the Co/Cu ratio on their physicochemical and catalytic properties in the hydrogenation of furfural.

In this work, the conditions for obtaining single-phase CoCuAl-LDHs by the coprecipitation method were optimized. Successfully synthesized CuAl- and CoCuAl-LDH with ratio Co/Cu= 1:2, 1:1 and 2:1 at pH=9.5 and temperature 60 °C. The structural properties of the obtained samples were studied by XRD. The process of formation of the oxide phase was studied by thermal analysis. The process of reduction of cobalt and copper from the formed oxide phase was studied by the TPR method. CoAl-LDH and CoCuAl-LDH were found to have two peaks of reduction in the TPR profiles. These peaks probably correspond to the reduction of metals from two types of mixed oxides of copper and cobalt. The CuAl sample has only one peak of reduction on the TPR profile with a maximum at 231°C. With an increase in the content of copper in the composition of the catalyst, the maxima of the peaks of reduction shift to lower temperatures. This may indicate the formation of bimetallic CoCu particles in the composition of catalysts based on CoCuAl–LDH. The catalytic properties of the samples were studied on a laboratory setup for the liquid-phase hydrogenation of furfural at elevated pressure. The dependence of the activity of the catalysts on the Co/Cu ratio as well as on the pretreatment conditions (different reduction temperatures) and the reaction conditions was established. Under mild reaction conditions ($T = 90°C$ and $p = 2.0$ MPa), catalysts based on CoAl-LDH showed high activity (89%) and high selectivity of furfuryl alcohol formation (98%). The activity of the catalysts decreased with an increase in the proportion of copper in the composition. This is probably due to the high reduction temperature (originally 800°C for all samples) at which the copper-containing particles sintered and coarsened.

The authors are grateful to Lysova E.I. for synthesis of catalysts.

The study was funded by the Russian Science Foundation grant № 22-23-20040, https://rscf.ru/en/project/22-23-20040/.

Synthesis and study of heterogeneous catalysts based on noble metal nanoparticle stabilized by ionic liquids

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Noble metal-based hydrogenation catalysts find many applications in petrochemical, green chemistry and fine chemicals processes. A significant disadvantage of highly active catalysts based on metal nanoparticles is their tendency to sinter during operation and regeneration, which leads to a decrease in activity. One of the ways to solve this drawback is the use of ionic liquids as a medium for stabilizing nanoparticles. Ionic liquids (ILs) are a low-temperature salt melts, usually formed by organic cations and inorganic anions, there was a hope that their use would help improve some catalytic processes and create fundamentally new technologies that meet modern trends in «green» chemistry [1]. Ionic liquids have received recognition in catalysis, but their use is limited by a number of problems associated with high viscosity and, as a result, low diffusion coefficients of the components of reaction systems. However, these drawbacks can be circumvented by immobilizing ILs on porous materials with a developed inner surface. Synthetic approaches, which consist in the introduction of the active component of a heterogeneous catalyst (salt, metal complex) into the layer of the supported IL precursor, followed by its reduction, make it possible to create catalytic systems that are highly dispersed metal particles fixed inside the support pores. Such a strategy for creating catalytic materials significantly reduces the consumption of both the IL itself and the expensive active component, most often a noble metal [2].

The topic of this research is the study of the features of the flow of hydroprocesses in the presence of heterogeneous catalytic systems based on ionic liquids.

We synthesized samples modified with the ionic liquid 1-ethyl-3-methylimidazolium diethylphosphate. The immobilization of ionic liquids on SBA-15, SiO_2 carriers was carried out according to the procedure described in [3].

The textural characteristics of the supports and catalysts were determined by nitrogen adsorption at 77 K on a Quantochrome Autosorb-1 adsorption porosimeter. The specific surface area was calculated using the BET method at a relative partial pressure P/P_0 of 0.05–0.3. The total pore volume and pore size distribution were determined by a desorption curve using the BJH model at a relative partial pressure P/P_0 of 0.99.

When metal is deposited on a silicon oxide support, the pore volume and specific surface decrease from 0.990 to 0.977 cm^3/g and from 360 to 331 m^2/g, respectively. For a sample additionally modified with an ionic liquid, a greater decrease in texture characteristics is observed: the pore volume and specific surface, compared to the unmodified sample, decrease from 331 to 280 m^2/g and from 0.977 to 0.862 cm^3/g, respectively. A similar dependence is observed on the SBA-15 support. And the synthesized catalysts were investigated by the methods temperature-programmed reduction (TPR) and high-resolution transmission electron microscopy.

Catalytic tests of the synthesized catalysts will be carried out on a laboratory flow unit with a fixed bed reactor in hydrogenation of biphenyl.

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Ce- and Cu-modified OMS-2 catalysts for low-temperature CO oxidation

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The complete oxidation of VOCs and CO, that are hazardous to humans is effectively carried out using catalysts, main component of which are noble metals. However, due to their high cost, noble metal replacement with more accessible metals remains the issue of the day. For this reason, it becomes expedient to search for an alternative to platinum- and palladium-containing catalytic complexes for low-temperature CO oxidation process.

Manganese dioxide with the octahedral molecular sieves (OMS-2) structure is one of the promising catalysts for complete oxidation of VOCs and CO [1]. High mobility of lattice oxygen due to presence of defects of doubly and triply charged manganese ions in the framework leads to a sufficiently high activity of pure OMS-2 in these processes. Catalytic activity of OMS-2 can be increased by its modifying with cations of various metals (Ag^+, Cu^{2+}, Fe^{3+}, Ce^{4+}, etc.) [2, 3]. Among metals of variable valence, cerium and copper are of the greatest interest due to peculiarities of the redox transitions Ce(III) ⇄ Ce(IV) in CeO_x [4] and Cu(II) ⇄ Cu(I) in Cu_xO [5].

Hydrothermal synthesis (HTS) is one of the methods to obtain cerium- and copper-containing OMS-2 (M-OMS-2, M = Ce, Cu) [6, 7]. The purpose of this work was to study effect of modifiers nature on the OMS-2 catalytic properties prepared by hydrothermal method in low-temperature CO oxidation, as well as to establish hydrothermal treatment conditions (pressure) effect on M-OMS-2 catalysts properties. Two series of catalysts #Ce and #Cu were prepared by HTS. For #Ce series, $KMnO_4+Mn(NO_3)_2+Ce(NO_3)_3+HNO_3$ (120 °C, 24 h), for #Cu series − $KMnO_4+Cu(NO_3)_2+NH_4Cl+HCl$ (200 ºC, 48 h). The synthesis pressure was controlled by filling autoclave with different amounts of mother liquid.

Results of elemental composition (XRF) and crystal structure (XRD and Raman spectroscopy) showed that there is a clear correlation between HTS pressure and amount of introduced modifier. Thus, pressure increase led to increase of metals content in the samples. In addition, higher pressure led to increased defectiveness of OMS-2 crystal lattice in copper series and almost complete rearrangement of OMS-2 structure in a cerium series. According to XRD and low-temperature nitrogen adsorption-desorption data (BET), samples obtained under more severe HTS conditions have higher phase dispersity and larger specific surface area of particles. Catalytic experiments on CO oxidation were carried out in a quartz reactor in temperature programming mode at molar ratio $O_2/CO = 8/1$ with GHSV of 90 000 h^{-1}. It was determined that in #Cu series, the catalyst synthesized at a higher pressure exhibits highest catalytic activity among the samples of both series. For both #Ce samples, catalytic properties are noticeably weaker, probably, due to lower content of OMS-2 phase. Further research will be focused on studying properties of Ce-OMS-2 catalysts prepared by modified procedure and properties of supported catalysts based on Cu-OMS-2.

This work was supported by Russian Science Foundation, grant № 19-73-30026.

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Synthesis of ethanol steam reforming catalysts based on $LaFeO_3/SiO_2$

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The ethanol steam reforming is the base for the future of hydrogen energy. Therefore, the search of catalysts for this reaction is of high importance nowadays. It was shown that lanthanum silicates with apatite structure (undoped and doped with iron and aluminium) have high catalytic activity in such oxidative processes as methane dry reforming and methane steam reforming. The purpose of our work is a synthesis of iron-doped lanthanum silicate with apatite structure and application to its surface praseodymium nickelate with Ruddlesden-Popper structure Pr_2NiO_4. Samples were synthesized by sol-gel method using tetraethoxysilane hydrolyzed with 0,1 M nitric acid with the addition of β-cyclodextrin and urea as a template. β-cyclodextrin is a cyclic oligosaccharide formed by seven D-glucopyranoside units linked with 1,4-glycosidic bonds. Its molecule has a hydrophilic external surface and hydrophobic internal cavity. This structure allows β-cyclodextrin molecules to form “host-guest” complexes and associate them into columnar structures, which promote the formation of desired size pores. The samples with 6.3 mas.% NiO, 11.8 mas.% Pr_4O_7, 50.8 mas.% $LaFeO_3$ and 31.1 mas.% SiO_2 were obtained. The influence of water amount used during the synthesis of mesoporous SiO_2 precursors on the properties of obtained catalysts was studied ($m(H_2O) = 5*m(SiO_2)$ for sample 5-NP and $m(H_2O) = 20*m(SiO_2)$ for sample 20-NP).

It was established by XRD that there is an amorphous phase based on apatite structure with a halo at 23–39° on the 2θ scale. Moreover, there are characteristic phase reflexes of $LaFeO_3$ (PDF ICDD 37-1493, PCPDFWIN, Version 2.2, June 2001, JCPDS-ICDD), Pr_7O_{12} (PDF ICDD 71-0341) and NiO (PDF ICDD 47-1049). Sample 5-NP was more crystallized than 20-NP.

Specific surface area analysis by BET and BJH methods showed main differences in the structure of samples. Sample 5-NP has $S = 37\ m^2/g$ and has mesopores, micropores and macropores. Sample 20-NP has $S = 52\ m^2/g$ and has only mesopores in its structure.

Temperature-programmed isotopic exchange with the use of $C^{18}O_2$ showed that 20-NP has higher volume mobility of oxygen. The mole fraction of substituted oxygen in the 20-NP sample was 31 % under 600°C. The mole fraction of substituted oxygen in the 5-NP sample was lower, 20% under 600°C. The exchange proceeds on mixed oxide fragments with cations of praseodymium and nickel under low temperatures. The exchange proceeds on mixed lanthanum/praseodymium ferrite/nickelate under medium temperatures. The exchange proceeds with oxygen in an iron-doped lanthanum silicate with an apatite structure under high temperatures. The diffusion coefficient was counted for the 20-NP sample. It is about $10^{-16}\ cm^2/s$ under 427°C.

Temperature-programmed reduction by hydrogen (H_2-TPR) showed that there are 3–4 H_2 consumption peaks in temperature interval 150–900°C. Furthermore, sample 20-NP requires more hydrogen for its reduction than 5-NP.

Samples were examined in ethanol steam reforming reaction with a mixture composition of 2 vol.% EtOH + 8 vol.% H_2O in helium and contact time of 10 ms. The samples worked stably under 550–650 °C with the growth of ethanol conversion from 35% to 60% with temperature and yield of hydrogen, which was defined by conjugation with CO steam conversion ($H_2/CO=5\div4,5$). The by-product was ~0,1% CH_4. The decline of reactivity was under 500°C because of carburization. The optimal conditions for stable catalyst work are reduction and reaction under 600°C. Sample 5-NP can work stably for only 1,5 hours. Then its reactivity falls due to carburization. Sample 20-NP can work stably in these conditions for more than 9 hours due to its greater reactivity and mobility of its oxygen.

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Pd-catalysts based on amino-containing porous aromatic frameworks for the semi-hydrogenation of alkynes and dienes

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Olefins are core building blocks for the production of synthetic rubbers, plastics, lubricants, and detergents. Transition metal-catalyzed selective hydrogenation of alkynes has been reported as a straightforward and effective route for alkene synthesis. Various noble metal-catalyzed systems have been developed and exhibited excellent activity in the semi-hydrogenation, with Pd ones being the most selective [1]. In addition to the metal catalytic center, it is also essential to choose the suitable catalytic support, which could immobilize metal nanoparticles and define its dispersion and electron effects. Furthermore, the interaction between the active metal and support materials plays a crucial role in enhancing the comprehensive catalytic activity [2].

Porous aromatic frameworks (PAFs) are a class of porous organic polymers constructed of aromatic rings, connected to each other by covalent C–C bonds. They demonstrate considerable potential applications in catalysis, owing to their high specific surface areas, chemical and physical stability and rigid structure [3]. Due to aromatic nature of PAFs, a wide range of well-known and relatively simple techniques of functionalization is available. Thorough selection of reagents and synthetic conditions allows to obtain materials with already implemented functionalities and structural characteristics tuned for the effective stabilization of metal nanoparticles, and maximum enhancement of their catalytic activity and selectivity. There are two approaches to the modification of PAFs: pre-modification, which involves the use of monomers with needed functional groups in the synthesis of the support, and post-modification, when previously synthesized material undergoes treatment to implement functional groups.

In the present work, we studied series of Pd-catalysts based on two amino-modified PAFs – **PAF-20-NH$_2$-post/pre** and **PAF-30-NH$_2$-post/pre** – with metal loadings of 2% and 5% in the hydrogenation of various unsaturated compounds with different chain length, including terminal and internal alkynes as well as dienes. Both frameworks were synthesized by combination of pre- and post-modification approaches [4]. At the first stage nitro-containing materials **PAF-20-NO$_2$-post** and **PAF-30-NO$_2$-post** were synthesized via Suzuki cross-coupling reaction using tetrakis-(4-bromo-3-nitrophenyl)methane and 1,4-benzenediboronic or 4,4′-biphenyldiboronic acid, respectively. Then they were additionally treated with nitric acid to introduce more nitro groups, which were subsequently reduced with tin (II) chloride in THF to obtain **PAF-20-NH$_2$-post/pre** and **PAF-30-NH$_2$-post/pre**. Synthesized materials were impregnated with solution of $Pd(OAc)_2$ in CH_2Cl_2, then the solvent was removed under reduced pressure and the metal was reduced with ethanol solution of $NaBH_4$.

All of the hydrogenation reactions were performed without solvents at 60 °C and 10 atm H_2. Concentration of the impregnating solution influenced the morphology of metal particles significantly, as the more concentrated solution contributed to the wider particle size distribution for **5%Pd@PAF-20-NH$_2$-post/pre** and **5%Pd@PAF-30-NH$_2$-post/pre**, while the amount of metal ended up being ~2% for each of the four catalysts, which indicated limited framework capacity. Common trend for all systems consisted in higher hydrogenation activity of internal alkynes and dienes over terminal alkynes. **5%Pd@PAF-20-NH$_2$-post/pre** proved to be the most active albeit least selective due to diffusion limitations in PAF-20 materials. **2%Pd@PAF-20-NH$_2$-post/pre** and **2%Pd@PAF-30-NH$_2$-post/pre** were slightly less active in the hydrogenation of terminal alkynes, but on the other hand, a bit more active for internal alkynes and dienes.

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Development and optimization of new glass fiber catalysts for the process of methanation of carbon dioxide with hydrogen

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One of the most urgent scientific and technical purposes in designing of a new energy industry with zero or reduced level of CO_2 emissions is the development of highly efficient energy conversion and storage technologies for damping of daily and weather variations in the production and consumption of electricity. The application of chemical cycles based on the catalytic transformations of carbon dioxide and hydrogen is the most effective way.

Significant progress in this field can be achieved through the use of catalysts based on microstructured supports [1]. The main advantage of such catalytic systems is the ability of forming of the structured cartridges with a uniquely high ratio of mass transfer intensity to specific hydraulic resistance [2, 3].

The aim of this research is to develop a simple and efficient technique for the preparation of the zeolite/glass fiber composites.

Heat-resistant fiberglass KT-11-TO was used as a support for the synthesis of glass fiber catalysts. The organic coating on the surface of the glass fabric was removed by calcination at 600°C for 2 hours before modification with a secondary. To develop the specific surface area of the support, a precursor of the secondary support of the MFI-type zeolite was prepared. Part of the source of SiO_2 is the fiberglass itself. Modification of the glass fiber material was carried out by the hydrothermal method in an autoclave at 110°C for 24 hours. The molar ratio in the final solution is $10Na_2O:100SiO_2:2Al_2O_3:2250H_2O$ that amounts to the MFI ZSM-5-type zeolite.

The XRD method was used to verify the phase composition of the zeolite. The morphology of the resulting zeolite was examined by SEM. After modifying the fiberglass with a secondary carrier, the ions of Ni, Co, and Ce were introduced into the zeolite structure by the ion exchange method. The sorption properties of the obtained composites were studied by the TGA method.

The study was carried out with the financial support of the Tyumen region as part of the implementation of the Grant Agreement in the form of a subsidy to non-profit organizations No. 89-DON dated back to December 7, 2020.

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Structure and properties of Ni(Cu)/$LaCeO_x$ catalysts

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Eco-friendly industrial processes are of great interest nowadays as they allow to obtain important chemical products with minimal impact on the environment. Dry reforming of methane (DRM) is one of such promising processes. Two most important greenhouse gases, i.e. CH_4 and CO_2, are converted into syngas to produce many chemicals such as liquid fuel, aldehydes, methanol, etc. It is widely known that Ni-based catalysts are the most effective for DRM but they tend to deactivate under high temperatures due to the coking. Different supports were proposed to stabilize Ni particles, increase the dispersity of metal and active site content. This leads to a higher catalytic activity and prolonged exploitation of the catalysts. Basic supports are in favor as the adsorption of CO_2 on their active sites decreases carbon formation by oxidation of surface carbon and increases the overall activity. The aim of the present work is to comparatively study the structure and basis properties of Ni/$LaCeO_x$ catalysts with different La:Ce ratios and with/without Cu addition in DRM reaction.

The supports $LaCeO_x$ with different La:Ce molar ratios (1:1 and 12:1) were prepared by citrate method and calcined at 700 °C. 10 wt.% Ni/$LaCeO_x$ catalysts were prepared by wetness impregnation using $Ni(NO_3)_2$ aqueous solution. The Cu dopants were impregnated likewise (1 mol.% or 20 mol.%, calculated per Ni amount). Structure and composition of catalysts were examined by N_2 adsorption method, XRF, XRD and Raman spectroscopy. The reducibility of Ni ions was studied by H_2-TPR method in the temperature range of 30–900 °C. The basicity of the supports and catalysts was investigated by CO_2-TPD adsorption method. The gradient temperature DRM tests were carried out by increasing the temperature from 400 °C to up to 800 °C. The reagent gas mixture consisting of 15 vol.% CH_4 + 15 vol.% CO_2 in N_2 was passed over the catalyst with a flow rate of 50 ml/min. Long-run tests at 650 °C for 6 h were carried out as well in order to study the stability. Spent catalysts were characterized using TGA and TG/DTA analyses.

According to XRD data, it was found that binary oxides $LaCeO_x$ formed a solid solution for both La:Ce ratios. The increasing of oxygen vacancy concentration led to the formation of C-type phase at La:Ce = 12:1. The C-type phase was partially preserved after the introduction of the active component. The nature of Ni-containing precursor formed over the support surface was found to depend on the phase composition of the binary oxide. The formation of lanthanum nickelate phases was observed for Ni(Cu)/$LaCeO_x$ (12:1), while for Ni(Cu)/$LaCeO_x$ (1:1) sample the presence of $Ce_{1-x}La_xO_{2-\delta}$ solid solution phase with the fluorite structure facilitated the NiO formation. According to the TPR-H_2 data, Ni in forms of NiO and lanthanum nickelates underwent reduction in the following temperature ranges: 300–400 and 200–600°C, respectively. The CO_2-TPD displayed high contents of strong basic sites for $LaCeO_x$ (12:1) sample and lower contents of weak and medium basis sites for $LaCeO_x$ (1:1) sample.

The Ni(Cu)/$LaCeO_x$ (1:1) catalyst showed the highest conversion of reagents ($X(CH_4) = 95\%$; $H_2/CO = 0.96$) but a slight deactivation of 1.4 rel.% occurring during the long-run test at 650 °C for 6 h. Despite lower values of the CH_4 and CO_2 conversions obtained for the Ni(Cu)/$LaCeO_x$ (12:1), its activity increased (by more than 9 rel.%) during the long-run test. For all catalysts, carbon deposition was observed, however, its amount was almost 2 times lower for the Ni(Cu)/$LaCeO_x$ (12:1).

This work was supported by Russian Science Foundation, grant № 19-73-30026.

Application of catalysts with added carbon nanotubes in processing of n-heptane

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Carbon nanotubes (CNT) are considered a very interesting material, especially after being discovered by Sumio Iijima in 1991. CNT have attracted great interest from the scientific community, due to their unique structural, mechanical, and electronic properties [1–2]. During several decades, a variety of emerging carbon supports for precious metal catalysts have been used in heterogeneous catalysis, such as carbon allotropes and shaped carbon nanomaterials, including carbon nanotubes [2–3].

The methods for doping carbon nanotubes on its surface include: a) intermolecular forces (π-stacking, electrostatic, hydrophobic or hydrogen-bond interactions); b) chemical methods (deposition with electrochemical techniques, chemical reduction, in situ growth of nanoparticles); c) physical methods (ion/electron beam irradiation, sputtering, evaporation deposition) [2].

Since the surface of the metal is available to catalyze a reaction, it is normally advantageous to maximize the metal surface area by synthesis of small nanostructures, typically between 1–10 nm, anchored to a thermally stable, high-surface-area support such as alumina (Al_2O_3), silica (SiO_2), titania (TiO_2), or carbon (C) [4].

The present work shows the synthesis procedure and functional characterization of a nanostructure network of platinum-based carbon nanotubes with alumina.

The deposition of platinum on carbon nanotubes was carried out by wet impregnation of hexachloroplatinic acid [5]. Prior platinum impregnation, the surface of multiwalled carbon nanotubes was functionalized with an acidified solution of nitric and sulfuric acid [3]. Pt-CNT powder was mechanically grinded with activated alumina and dissolved in absolute ethanol by sonication.

The physicochemical characteristics of the composite-catalysts were studied by the following methods: BET (the Brunauer–Emmet–Teller method), EDX spectroscopy (Energy-Dispersive X-ray), and Transmission electron microscopy (TEM).

The BET surface area of the catalyst was 148.8 $m^2 \cdot g^{-1}$, which was determined with nitrogen physisorption. The Transmission electron microscopy data showed that platinum nanoparticles does not appear uniformly and homogeneous distributed over the surface of the catalysts, a result expected due to the low BET surface area value.

The Energy-Dispersive X-ray spectrum taken from the composite (Pt-CNT/alumina), displays that only oxygen and aluminium peaks are present, revealing that the carbon nanotubes are completely covered by Al_2O_3. These results are in agreement with the findings reported previously [6].

The study of the catalytic activity was performed using n-heptane, which was reformed in a tubular fixed bed reactor system (Microcatatest MCB 890, Vinci Technologies, France), under hydrogen flow, with a n-heptane:H_2 ratio of 1:5, temperature of 430°C and pressure of 24 barg.

The conversion of n-heptane was found to be 77.3% within 240 minutes time-on-stream. The GC chromatography results show that the tendency to isomerization was through the formation of methylhexanes and dimethylpentanes, which shows a possible application in the processing of gasoline fractions. Although the reaction conditions applied to study the catalyst were typical of catalytic reforming, Pt-CNT/alumina catalyst exhibited higher selectivity to isoparaffins of C7 group (single and double branched isomers).

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Low temperature CO oxidation over ternary oxide Ag_2CuMnO_4 under wet conditions

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Efficient low-temperature catalytic oxidation of air pollutants such as carbon monoxide and volatile organic compounds is an important task of heterogeneous catalysis. Catalytic systems based on oxides of transition metals are promising materials due to their efficiency and low cost. The investigation of catalytic activity and physicochemical properties of mixed oxide Ag_2CuMnO_4 with delafossite structure was our aim in this work.

For preparation of catalysts the hydrothermal synthesis of Ag_2CuMnO_4 using widely available precursors [1] was proposed. Application of XRD allowed reliable evidencing that single-phase delafossite (3R-Ag_2CuMnO_4) was obtained without other crystalline phases. XPS investigation was occurred in order to determine the composition and charge states of metals on the surface. Using XPS it was shown that silver is presented in ionic Ag^+ state, copper was found to be in Cu^{2+} state and manganese is proved to be Mn^{4+} with the partial presence of reduced states (Mn^{2+} and/or Mn^{3+}). Quantitative XPS analysis indicates manganese enriched and copper depleted Ag_2CuMnO_4 surface.

Ag_2CuMnO_4 exhibited catalytic activity for CO oxidation at temperatures below 0 °C. Value of specific catalytic activity of CO oxidation was estimated to be $1.7\cdot10^{11}$ molecules$\cdot$cm$^{-2}\cdot$s^{-1} and activation energy was equal to 25 kJ/mol. It was also found that in the presence of water vapor (in the mixture 0.01% CO/ 5% O_2/ 4% H_2O/He) ternary oxide was able to realize catalytic oxidation of carbon monoxide for more than 5 hours. It implies that prepared ternary oxide demonstrates higher stability and durability than well-known hopcalite catalyst, which significantly deactivates during 20 min of reaction [2].

In order to improve the catalytic properties, we optimized the preparation conditions. It revealed that increase of pH value of synthesis solution led to larger size of delafossite crystallites causing the lessening of catalytic activity in wet CO oxidation. Samples synthesized in the range $10<pH<12$ contained CuO particles and amorphous phase in the addition to delafossite particles. Such samples exhibited two times higher value of specific catalytic activity in wet CO oxidation at 25 °C compared to pure delafossite phase samples. The most active catalysts didn't demonstrate any deactivation after 6 hours of reaction, while the absence of delafossite phase in ternary Ag-Cu-Mn system resulted in the drop of specific catalytic activity by one order of magnitude. Also increase in temperature of hydrothermal synthesis led to degradation of catalytic activity due to a dispersion decrease.

Thus, ternary oxide Ag_2CuMnO_4 is highly promising catalytic material with a great potential for low-temperature oxidation reactions. Investigation of Ag_2CuMnO_4 as novel catalytic material with improved efficiency is of interest for the development of fundamental aspects in the field of oxidative heterogeneous catalysis. Both the improved catalytic properties and the relatively low cost of the delafossite based system provide great potential for industrial applications.

This work was supported by the Ministry of Higher Education and Science of the Russian Federation, Grant MK-503.2021.1.3.

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One-pot synthesis of granulated alumina-chromia catalysts for fixed-bed isobutane dehydrogenation

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The demand for olefins continues to grow rapidly that is associated with a growing manufacturing of polymers and other chemicals. In the Russian petrochemical industry, the microspherical alumina-chromia fluidized-bed catalysts are mainly used for the dehydrogenation of paraffinic hydrocarbons into the corresponding olefins [1]. The processes of dehydrogenation of paraffins with a fixed catalyst bed (Catofin and Catadiene processes are practically not implemented in Russia because of the lack of Russian-made fixed-bed catalysts.

High requirements are imposed to fixed-bed catalysts: they should feature high activity and selectivity, be resistant to catalytic poisons, withstand short-term overheating, have high stability, including maintaining high catalytic activity and pellet strength for a long operation time (more than 1 year [2]. Particular attention is paid to the porous structure of the catalyst since it determines the catalytic properties of the catalyst granules. For high-temperature processes such as the dehydrogenation of paraffins, which proceed with an increase in the number of moles of a substance and are limited by thermodynamic equilibrium, the porous structure significantly affects the process performance since it determines the mass transfer inside the catalyst granule [3,4]. The development of supports and catalysts with a biporous structure, including meso- and macropores, is a promising solution. One-stage wet mixing method of catalyst preparation may be an alternative to the impregnation method for the industrial implementation of the synthesis of alumina-chromia catalysts. This method is based on the preparation of catalysts directly from the precursors of support, active component, and modifiers, followed by extrusion and heat treatment. This approach can significantly reduce the number of stages and, accordingly, energy costs. The development of methods to control the structure of alumina-chromia catalysts, in particular, the creation of a biporous (hierarchical pore structure, is an important challenge to create catalysts that meet the requirements of industrial application in dehydrogenation in a fixed-bed reactor.

A series of chromium-containing catalysts was synthesized by wet mixing. Alumina precursor (thermally activated aluminum trihydroxide was mixed with an aqueous solution containing dissolved precursors of chromium oxide (CrO_3, chemically pure and modifier (KNO_3, chemically pure. Wood flour was used as a porogen agent in an amount of 2 to 8 wt.%. Then, the resulting mass was molded by extrusion to obtain cylindrical granules with a diameter of about 3 mm. The catalyst was dried at a temperature of 100°C for 4 h and calcined in air at 750°C for 4 h. It was shown that the addition of a wood additive made it possible to obtain catalyst granules with the biporous structure (the presence of meso- and macropores. Wood flour did not affect the phase composition and distribution of chromium in the catalyst. The catalytic properties of the composites obtained by the one-stage wet mixing method were close to those of the catalysts obtained by the impregnation method. The isobutane conversion of 60–68% with the selectivity towards isobutylene of above 93% were achieved at 570-610 °C over alumina-chromia catalysts synthesized by the one-pot wet mixing method.

The work was carried out within the framework of the state task of the Ministry of Education and Science of Russia (project no. 0721-2020-0037).

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Development of technology for producing silica from diatomite and other Si-containing materials

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Silica (SiO_2) is a material widely used as a sorbent, desiccant, catalyst support, etc. Nevertheless, more than 50 thousand tons of silica are imported into Russia annually as a filler for tires and rubber products (~58%), as a filler for pet trays (~22%), for the production of cosmetics and toothpastes (~8%), for beer filtering (~4%), for building industry (~3%), for paints and varnishes (~1.5%), etc. [1]. Currently, the silica production in the Russian chemical industry is based on the developments of the 1950–1960s. The current Russian technology to produce silica is based on a complex technological cycle which is multi-stage and energy-consuming and also should also meet high safety requirements. The quality of many domestic products is lower as compared to imported analogues. The aim of this study is to develop a technology for silica production from available Si-containing materials: diatomite and industrial wastes.

The dissolution of Si-containing materials (diatomite and Si-stoff) was carried out using NaOH to obtain liquid glass. The obtained liquid glass was used to synthesize a series of silica of various grades. The structure of diatomite and silica samples was studied by the low-temperature N_2 adsorption-desorption and scanning electron microscopy (SEM). The elemental analysis was carried out to determine the concentration of impurities in diatomite and other Si-containing materials.

The SEM results showed that the initial diatomite powder consisted of disc-shaped and cylindrical structures, numerous pores were clearly visible that indicated high porosity and a relatively large specific surface area of diatomite [2]. The method of low-temperature nitrogen adsorption showed that the initial diatomite was characterized by a mesoporous and macroporous structure with pores of 10–100 nm. The specific surface area of the used diatomite was 46 m^2/g and the pore volume was 0.09 cm^3/g.

To obtain liquid glass, diatomite and Si-stoff were used. The content of SiO_2 in diatomite and Si-stoff was 80–98% [3]. At the initial stage, the SiO_2 leaching from diatomite and Si-stoff was carried out using NaOH to obtain liquid glass with a SiO_2 concentration of 200 g/l and a silicate module of ≈ 3 at room temperature and under heating. According to the developed method, the degrees of dissolution of diatomite and Si-stoff grew with an increase in temperature and duration of the dissolution achieved ~40–80%.

To synthesize a series of silicas, the liquid glass obtained by dissolution of diatomite and Si-stoff was precipitated with mineral acids. It was shown that the pH value of precipitation was the key parameter that determined the porous structure of the resulting silica gel. The series of silicas, synthesized from Si-stoff, were characterized by specific surface area from 129 to 353 m^2/g and the series of diatomite-derived silicas were characterized by a specific surface area from 52 to 420 m^2/g.

Thus, a method has been developed to obtain the liquid glass from available Si-containing materials such as diatomite and Si-stoff for further production of silica of various grades. The results of scanning electron microscopy and low-temperature nitrogen adsorption indicated the presence of a developed porous structure of the initial diatomite, which can be used to improve the characteristics of the prepared silica. Moreover, wide opportunities to control the porous structure of SiO_2, its relative inertness, low cost as well as the high need in import substitution of silica-based sorbents and catalysts, encourage the research in this area and the development of technologies to produce new SiO_2-based functional materials.

This work was supported by the Ministry of Education and Science of Russia (project no. 0721-2020-0037).

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SECTION 2

PROMISING CATALYTIC PROCESSES

Influence of the Si/Al ratio on the ratio of isomerization/cracking reactions in the hydroisomerization of fatty acids triglycerides

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A promising direction in oil refining is the use of biorenewable sources of raw materials, such as technical vegetable oils. Vegetable oils can be involved in hydroprocesses aimed at the production of high quality fuels. Thus, the involvement of fatty acids triglycerides in the process of hydroisodeparaffinization of diesel fractions will make it possible to obtain high-quality arctic diesel fuels. However, traditional catalytic systems based on Co(Ni) and Mo(W) metals deposited on a porous support, γ-Al_2O_3, do not allow one to obtain a product of the required quality.

One way to improve the characteristics of the catalyst is to introduce a zeolite additive into the support. Zeolites are highly active in reactions proceeding by the mechanism of carbenium ions due to active acid sites. Isomerization reactions are preferred in the hydroisodparaffinization process. However, undesirable cracking reactions also occur at acid sites. The effect of the Si/Al ratio on the selectivity of isomerization/cracking reactions in the process of hydroisodparaffinization of fatty acid triglycerides was studied in this work.

To study the effect of the zeolite component, commercially available zeolites with three silica-alumina ratios 30, 60, and 80 were used. They were used to prepare supports based on AlOOH pseudoboehmite by co-extrusion with nitric acid used as a peptizing agent. The amount of each zeolite in the support was 10%. The supports were analyzed by porosimetry. It has been established that with an increase of the silica-alumina ratio of the zeolite, the specific surface area and pore volume of the support increase. At the same time, the surface area and micropore volume increase.

Further, catalysts were prepared on the basis of the obtained supports. Nickel citrate and phosphomolybdic acid were used as active phase precursors. The catalysts were obtained by wetness impregnation. The finished catalysts were examined by TPD, porosimetry, TEM, XPS, XRD, and FTIR of adsorbed pyridine. The catalytic activity of the obtained catalysts was analyzed in the hydroisomerization process on a laboratory flow unit.

As a result of the research, it was found that the use of a zeolite additive in the catalyst makes it possible to obtain a feedstock conversion in HDO reactions of 100%. However, it has also been found that an increase in the Si/Al ratio leads to an increase in the proportion of isomerization reactions relative to cracking reactions. In addition, it was found that the use of a zeolite with a high silicate modulus leads to a decrease in catalyst activity, which is associated with a decrease in the amount of active acid sites.

The study was financially supported by the Russian Science Foundation (project no. 21-79-10140, https://rscf.ru/project/21-79-10140/).

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Influence of preparation method of bismuth silicates/oxides materials on photocatalytic performance

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Different approaches are in use for removal of the dyes in wastewater. Photocatalysis is an attractive method for dye degradation since it requires only presence of the photocatalyst and light. Unlikely, other oxidation methods occur at high temperatures or pressures or additional oxidizing agent [1]. Bismuth metasilicate Bi_2SiO_5 has layer perovskite-type structure that promotes a spatial separation of the charge carries that ameliorates photocatalytic properties.

The report is focused on influence of preparation method of bismuth silicate/oxide materials on their phase composition, structure, optical and photocatalytic properties.

Photocatalysts were synthesized via 3 methods: mechanochemical activation (MA), solvothermal treatment (+ post-processing with impulse laser ablation (ILA)), and sol-gel. The atomic ration of Bi to Si in samples was mainly 2 to 1. When sol-gel technique was used, the ratio Bi/Si varied as following: 2.09/1, 2/1, 2/1.5.

Characterization of the samples were implemented with the use of XRD (and *in situ*), XRF, IR and Raman spectroscopies, SEM, UV-Vis DRS, TG-DSC. The features of the processes at the semiconductor/liquid interface were studied by electrochemical methods. Moreover, quantum-chemical simulation in OpenMX software package made it possible to predict structure of composite materials as well as its effect on optical properties. Photocatalytic performance was estimated in photodegradation of Rhodamine B (RhB) solution under Xe arc lamp irradiation.

Sample prepared via MA and subsequent thermal treatment at 600 ˚C for 2 h consisted of Bi_2SiO_5 and $Bi_{12}SiO_{20}$ phases identified by IR spectroscopy. The sample demonstrated 29% conversion of RhB degradation for 4 h. Despite the advantages of the method such as absence of solvents, more low temperature of phase formation compared to conventional solid-state approach, the material showed low photocatalytic activity due to poor value of S_{BET} (1 m^2/g).

Hydro/solvo-thermal treatment with following calcination allows preparing the samples with specific surface area up to 10 m^2/g. The sample prepared via solvothermal treatment absorbed the visible light up to 550 nm due to the presence of bismuth beta-oxide. The multiphase composition of the sample, namely, Bi_2SiO_5, $Bi_{12}SiO_{20}$, α-Bi_2O_3, β-Bi_2O_3, led to the highest photocatalytic activity in these series: 75% conversion of RhB through deethylation mechanism. Further post-processing of the photocatalyst by ILA increased the S_{BET} to 34 m^2/g but decreased the activity to 25% conversion. It is caused by high defectiveness of the composite structure that enhanced the recombination process but worsened the photocatalytic activity. The most active photocatalyst was synthesized via sol-gel technique in the study. Composite materials prepared with varying of synthetic conditions were characterized with S_{BET}=10-100 m^2/g. It was important to notice that the key role in the activity was played by the phase composition, and not by S_{BET}. Thus, the sample consisted of Bi_2SiO_5, α-Bi_2O_3, $Bi_{12}SiO_{20}$, β-Bi_2O_3 (35 m^2/g) showed higher photocatalytic performance that β-Bi_2O_3/Bi_2SiO_5 sample (100 m^2/g) or the sample prepared by solvothermal treatment. Additionally, this sample with the highest photoactivity is characterized with higher current intensity in dye solution compared to the sample synthesized with solvothermal treatment.

The comparison of activity for prepared samples with ones from literature as well as the details on phase formation common for each of the approaches will be also discussed. Additional measurements concerning conduction and valence bands positions for prepared photocatalyst, as well as detailed results of photoelectrochemical measurement (EIS, CVC) in different media will be discussed in report.

This work was supported by the Russian Science Foundation, grant No. 19-73-30026.

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Ammonia decomposition Ru-Ba/ANF catalysts for hydrogen energy

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The role of hydrogen as an energy carrier in the future may become one of the most sighnificant ones. However, the production of pure hydrogen requires the use of highly efficient catalysts capable of operating at relatively low temperatures.

One of the promising catalyst supports is γ-alumina nanofibers (ANF) [1]. The most active catalysts for the decomposition of ammonia were obtained on carbon carriers [2], so we prepared catalysts on ANF and ANFC (ANF with carbon coating) [3]. A series of Ru-Ba/ANF catalysts was prepared on those supports. Ruthenium catalysts were prepared by impregnation of ANF or ANFC with a solution of $[Ru(NH_3)_nCl_m](OH)_p$, reduction in H_2 stream at 450 °C, followed by impregnation with $BaCl_2$ and $Ba(CH_3COO)_2$ solutions and successive heating in Ar and H_2 at 450 °C.

These samples were characterized by X-ray diffraction analysis (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The catalytic activity in ammonia synthesis was determined by chromatography with a column filled with Haeyesep C sorbent, as well as by back titration of the H_2SO_4 solution, through which the gas mixture flow after the reactor was passed.

According to SEM results ruthenium is evenly distributed across all samples. Barium forms clusters of crystals on the surface due to the absence of spherical pores. It was not possible to detect clusters of crystals of barium compounds by the TEM method. The TEM results demonstrate the uniform distribution of active component particles on the surface of the alumina fibers for both pure and carbon coated supports. However, on the ANFC support, ruthenium particles cover all nanofibers, while nanofibers without nanoparticles were found on ANF. Their size, determined from TEM images, does not exceed, with some exceptions, 4 nm.

To determine the catalytic properties of the samples, tests were carried out in the decomposition of ammonia in a flow reactor with a fixed bed at a temperature of 400–500 °C and atmospheric pressure. Ruthenium on ANFC shows a higher activity in comparison with ANF sample. Moreover, this is true for both non-promoted and promoted samples (at T = 500 °C, 44.9 mmol $H_2/g_{cat}\cdot$min for Ru/ANFC versus 14.9 mmol $H_2/g_{cat}\cdot$min for Ru/ANF; 43.7 mmol $H_2/g_{cat}\cdot$min for Ru-Ba(Cl)/ANFC versus 17.8 mmol $H_2/g_{cat}\cdot$min for Ru-Ba(Cl)/ANF and 58.3 mmol $H_2/g_{cat}\cdot$min for Ru-Ba(Ac)/ANFC versus 32.8 mmol $H_2/g_{cat}\cdot$min for Ru-Ba(Ac)/ANF).

This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the governmental order for Boreskov lnstitute of Catalysis (project AAAA-A21-121011390009-1).

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C–H oxygenation of cycloalkanes and alkylbenzenes catalyzed by nickel(II) complexes with N4-donor ligands

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Direct selective oxygenation of non-activated C–H bonds is a challenging goal of synthetic chemistry; having efficient and versatile C–H oxygenation methodologies in hand is expected to revolutionize the synthesis of complex molecules, such as functionalized metabolites and related products of pharmaceutical and fine chemical industries [1]. In nature, O_2 is used as oxidant for C–H hydroxylation catalyzed by copper- and iron-containing oxygenases such as cytochrome P-450 and methane monooxygenase. For laboratory-scale oxygenation reactions, organic peroxides are convenient oxidizing reagents that do not require using stoichiometric co-reductants. Due to relatively low O–O bond dissociation energy, activation of peroxides leads to reactive radical species that can abstract hydrogen atoms from aliphatic C–H bonds. The carbon-centered radicals stemming therefrom are capable of trapping dissolved oxygen, eventually affording oxygenated products [2]. Engaging transition metal based catalysts potentially allows achieving much higher chemo- and regioselectivity in C–H oxygenation. In recent years, nickel(II) complexes with tri-, tetra- and pentadentate chelating ligands have been reported to be catalytically active in alkane hydroxylation with *meta*-chloroperoxybenzoic acid (*m*-CPBA); however, those in most cases ensured poor substrate conversions [3].

In this work, we present highly efficient selective oxygenation of cycloalkanes and arylalkanes with *m*-CPBA, catalyzed by nickel(II) complexes $[(L)Ni^{II}(CH_3CN)_2]X_2$ (1 mol.% loading) with N4-donor ligands BPMEN and TPA (BPMEN = N,N′-dimethyl-N,N′-bis(2-pyridylmethyl)-1,2-diaminoethane; TPA = tris(2-pyridylmethyl)amine; X = BPh_4, ClO_4, OTf) under mild conditions (room temperature, several hours reaction time). The structure of novel complex $[(BPMEN)Ni^{II}(CH_3CN)_2](OTf)_2$ was determined by XRD analysis, other Ni complexes was described previously.

In CH_3CN, the reaction occurs selectively at benzylic or 3° C-H groups, yielding the corresponding alcohols and ketones with up to 50% conversion. Structure of reaction products was determined by GC-MS.

Crucially, replacing acetonitrile as solvent with β-polyfluorinated alcohols drastically enhances the conversion of all studied substrates (up to 97%, using 1:1 substrate/oxidant ratio). Furthermore, in this case, the reaction predominantly yields β-polyfluoroalkoxy ethers. In case of ethylbenzene oxidation, the ratio of CH_2 mono-oxygenated products to acetophenone was as much as 17.5. The mechanism of C-H hydroxylation and/or alkoxylation, as well as the effect of ligand structure on the catalytic performance are discussed.

This work was supported by the Russian Science Foundation, grant 22-13-00225.

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Photocatalysts based on $Bi_{12}SiO_{20}$ for water purification from organic pollutants

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Pollution of industrial wastewater with difficult-to-oxidize compounds (phenol derivatives, dyes, antibiotics) has a negative impact on the environmental situation. In recent years, photocatalytic water purification methods have attracted increasing attention due to the ability to decompose organic compounds into harmless H_2O and CO_2 molecules. Bismuth silicates (BSO) [1, 2], in particular bismuth sillenite $Bi_{12}SiO_{20}$ [3], are considered a promising semiconductor photocatalysts. In the main, BSO is obtained by chemical synthesis methods that require the use of high temperatures and pressures during synthesis, as well as additional precursors. In this work, semiconductor nanoparticles (NPs) based on $Bi_{12}SiO_{20}$ with high photocatalytic activity were synthesized via pulsed laser ablation (PLA) in water.

The synthesis of BSO was carried out according to the technique described in [1]. The resulting powders were annealed at temperatures at 400 °C and 600 °C. The initial BSO_ini sample consists of metallic Bi and bismuth carbonate $Bi_2(CO_3)O_2$. Upon annealing at 400°C, the β-Bi_2O_3 and $Bi_{12}SiO_{20}$ phases form in the BSO_ini_400 sample. After laser treatment, the $Bi_{12}SiO_{20}$ phase, as well as $Bi_2(CO_3)O_2$, is formed in the initial sample without annealing BSO_hν. Annealing at 400°C leads to an increase in the percentage of the $Bi_{12}SiO_{20}$ phase from 26 to 77%. The samples after annealing at 600 °C are represented by the $Bi_{12}SiO_{20}$ phase with a small impurity (~2%) of the Bi_2SiO_5 phase. According to UV-vis spectroscopy, all samples (besides for BSO_ini) have the edge of the exciton absorption band in the visible region of the spectrum.

Photocatalytic (PC) activity was measured by the decomposition of Rhodamine B (5 μM), Phenol (50 μM) and Vancomycin (0.17 mM) under irradiation with a LED with λ = 375 nm (51 mW). The reaction rate constant was calculated taking into account the concentration of organic compound in units of [$\mu M \times h^{-1}$]. When evaluating the photodecomposition of Rhodamine B, the rate constants of K_N diethylation (from the decrease in optical density at 553 nm) and K_{app} decomposition (from the decrease in optical density at the absorption maximum) of the dye were calculated. When evaluating the PC activity of Phenol, the reaction rate was estimated from a decrease in the luminescence intensity. The decomposition of the initial Vancomycin molecule was determined by the relative decrease in the absorption band of aromatic fragments of the molecule at 280 nm.

During the decomposition of Rhodamine B, the samples after annealing at 600 °C showed the highest PC activity – K_N was 25.5 and 12.0 $\mu M \times h^{-1}$ for BSO_ini_600 and BSO_hν_600, respectively. In addition, it was found that laser treatment of the colloid leads to stability of the photocatalyst for 10 or more cycles. Samples BSO_ini_600 (K = 36.0 $\mu M \times h^{-1}$) and BSO_hν_400 (K = 30.0 $\mu M \times h^{-1}$) showed the highest PC activity during the decomposition of Phenol. During the decomposition of photostable Vancomycin, the samples after laser treatment with BSO_hν_400 and BSO_hν_600 showed the highest PC activity – the K values were 6.3 and 7.3 $\mu M \times h^{-1}$, respectively.

Thus, in this work, NPs based on bismuth sillenite $Bi_{12}SiO_{20}$ were successfully obtained via PLA method in water. It has been established that the best photocatalytic activity during the decomposition of Rhodamine B, Phenol, and Vancomycin is exhibited by samples with a high percentage of $Bi_{12}SiO_{20}$.

This work was supported by the Russian Science Foundation (Grant No 19-73-30026).

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Ceria-zirconia supported platinum catalysts for water gas shift reaction: The role of reaction conditions and catalyst composition

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Hydrogen energy is a topic actively discussed worldwide as a perspective way to reduce the emission of greenhouse gases into the atmosphere. There are a number of different approaches to produce hydrogen: water splitting, steam conversion of methane, biomass gasification, etc. The latter two yield to the hydrogen-rich gaseous product which contains 10–30 vol.% CO. Actually, CO removal is necessary to use this product to feed proton-exchange membrane fuel cells (PEMFC) generating electricity by means of electrochemical H_2 oxidation reaction at relatively low temperatures (< 60 °C). Water gas shift reaction (WGSR) is one of the processes of CO removal from hydrogen-rich gas. In this reaction, CO and steam are converted to H_2 and CO_2.

The industrial implementation of WGSR involves two sequentially connected reactors. In the first one, the reaction is carried out at high temperatures (300–500 °C) catalyzed by the iron-chromium oxide systems. After cooling down, the reaction mixture from the first reactor goes to the second, where the process is performed at low temperatures (150–300 °C) in the presence of a copper-zinc oxide catalyst. Although such a system makes it possible to reduce CO concentration to 0.5 vol.%, it is not suitable for portable energy generators [1], as well as the catalysts used are pyrophoric and require a long time activation procedure. So, noble metal-based catalysts were suggested to avoid these issues.

Platinum catalysts supported on ceria are reported to be one of the most active systems for WGSR. In this study, $Pt/Ce_{0.75}Zr_{0.25}O_2$ catalysts were prepared by sorption-hydrolytic deposition and tested in WGSR in reformate-simulating mixtures at 200–350 °C and ambient pressure. The influence of CO and H_2O inlet concentrations on the methane formation was studied. It was shown that the higher H_2O concentration is, the less CH_4 is formed via methanation side reaction. At the same time, decreasing CO concentration at a fixed H_2O content did not led to a significant decrease of CH_4 content. For 5 wt.% $Pt/Ce_{0.75}Zr_{0.25}O_2$ catalyst, the Pt and Ce charge dynamics in the reaction conditions was detected by means of quasi *in situ* XPS studies. Also, it was proved using TEM and XRD that the supported Pt particles are highly dispersed (1–2 nm) with a narrow size distribution and remain stable under WGSR conditions.

Bimetallic Pt-Re and Pt-Fe catalysts supported on $Ce_{0.75}Zr_{0.25}O_2$ were also prepared and tested in WGSR in the same conditions. It was shown for the catalysts with the atomic ratio Pt:M = 1:1 (M = Re, Fe) that Re enhances the activity of the catalysts, while Fe enhances the selectivity suppressing the reaction of carbon oxides methanation. The influence of Pt:M atomic ratio was also studied.

The work was supported by the Russian Science Foundation under the Project № 21-73-20075.

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Hydrolysis-hydrogenolysis hemicelluloses to ethylene or propylene glycol over cesium salts of heteropoly acid catalysts

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Ethylene- and 1,2-propylene glycols (EG and 1,2-PG) are widely used in industry as components of antifreezes and brake fluids, and are also used for the synthesis of polyesters. Moreover, propylene glycol is food additive E 1520. Fossil hydrocarbon sources are traditionally used for EG and PG production. The literature shows the possibility of obtaining glycol from plant biomass or its components. Glycols can be obtained by hydrolysis-hydrogenolysis of polysaccharides. The transformation of the polysaccharide is carried out in two stages. At the first stage, the polysaccharide is hydrolyzed to monosaccharides. At the second stage, the monosaccharide is hydrogenated to EG and PG via retro aldol cleavage into C_2-C_4 carbohydrates. One-pot performance of these steps requires the use of bifunctional catalysts. The most promising bifunctional catalysts for the hydrolysis-hydrogenolysis of polysaccharide are W-containing catalytic systems [1, 2].

The aim of this work was the development of bifunctional catalysts for the hydrolysis-hydrogenolysis of hemicellulose in EG and PG based on nickel or ruthenium supported on cesium salt of heteropoly acid (Ru/CsHPA, Ni/CsHPA). Ni and Ru deposited on CsHPA in the amount of 1 and 3 wt.%. The obtained catalysts were studied using a complex of physicochemical methods (IR, DR UV-vis, TEM, nitrogen adsorption, pH_{ZERO}, XPS).

It has been shown that the specific surface area for Me/CsHPA systems was in the range of 120–180 m^2/g. The introduction of Ni or Ru onto the CsHPA samples led to a decrease in the specific surface area. IR spectroscopy and XRD of Ru/CsHPA and Ni/CsHPA show no changes structures after the precipitation of Ru or Ni on CsHPA. According to TEM data, the particle size of ruthenium on CsHPA was 0.9–1.4 nm. According to the DR UV-vis, the spectra of the Ni/CsHPA and Ru/CsHPA samples show the appearance of a broad band in the area of 400–600 nm and 300–500 nm respectively, which indicates the appearance of a nickel and ruthenium metal phase. The intensity of this bands increases with the amount of deposited metal. XPS data showed for nickel to be both metal and oxide in the Ni/CsHPA samples. The surface acidity of the samples measured by pH_{ZERO} was in the range of 5–9.7. Acid and base centers of Ni/CsHPA catalysts were studied by IR spectroscopy using $CDCl_3$ as a probe molecule. In the IR spectra of samples, a band at 2255 cm^{-1} is observed, which characterizes the interaction of the $CDCl_3$ molecule with the basic centers. Supporting of Ru on CsHPA leads to decrease amount of the Brønsted acid sites, but to increase the amount of the Lewis acid sites [3].

The catalytic properties of catalysts were investigated in a high-pressure autoclave at 245 °C under H_2 atmosphere. The main reaction products were EG and PG, the by-product was glycerol. 3% Ni/CsHPA catalyst are more active than Ru/CsHPA. The maximum total yield of EG and PG reached 42 mol.% in the presence of 3% Ni/CsHPA catalyst under optimal conditions.

This work was supported by Russian Foundation for Basic Research Grant № 20-03-00263.

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Preferential CO oxidation in H_2: effect of modification by copper and manganese on catalytic performance of ceria-silica templated systems

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Ceria is a promising alternative for precious metal catalysts in oxidation processes due to its unique redox properties, relatively high thermal stability, and low cost. Such catalysts are promising for preferential CO oxidation (PROX-CO) required for effective CO removal from H_2-rich streams below the 10−100 ppm of CO-tolerance level accepted for proton exchange membrane fuel cells [1]. The catalytic performance of such oxide systems can be tuned using additives improving textural and structural properties [2, 3], and by addition of a second active component. In our work we used silica as a texture stabilizer, and CuO_x or MnO_x as a second active component to investigate the effect of the addition and the nature of the modifier on the catalytic efficiency in PROX-CO.

CeO_2-SiO_2 (Ce:Si = 4:1) was prepared by template method using cetyltrimethylammonium bromide (CTAB) and tetraethoxysilane (TEOS), and calcined at 500 ºC for 4 h. Cu or Mn (nominal metal loading was 5 wt.%) were supported by deposition-precipitation method using metal nitrates as precursors. The prepared systems were designated as Cu/CeSi and Mn/CeSi. Catalytic tests in PROX-CO were performed on the catalytic unit equipped with fixed-bed continuous-flow stainless steel reactor in the temperature range from 50 to 450 °C using 150 mg of catalyst and the reaction mixture comprising 4 vol.% CO, 3 vol.% O_2, 13 vol.% N_2 and 80 vol.% H_2, at 95 ml/min. The composition of the effluent was analyzed by GC using Carboxen-1010 PLOT capillary column.

Catalytic tests demonstrated that both Cu/CeSi and Mn/CeSi systems were active in PROX-CO. Despite the same metal content, CO and O_2 conversion, as well as CO_2 selectivity over Cu/CeSi were significantly higher than for Mn/CeSi over the entire studied temperature range. The highest CO conversion (77%) at a sufficiently high CO_2 selectivity (60%) was achieved on Cu/CeSi at as low temperature as 200ºC. The reasons for this behavior were established using TPR-H_2 data. The position of high-temperature reduction peak (~760–780 ºC) associated with the reduction of subsurface and bulk Ce^{4+} was almost the same in the H_2-TPR profiles of both catalysts, but the position of low-temperature peaks of Cu or Mn reduction were different. The TPR-H_2 profile of Cu/CeSi comprised one low-temperature peak centred at 201ºC with small shoulder at 182 ºC, indicating the presence of highly dispersed copper oxide species in contact with silica and ceria particles, respectively. The TPR profile of Mn/CeSi contained several less intense low-temperature reduction signals, which can be associated both with the stepwise reduction of manganese in different oxidation states and with the reduction of surface and subsurface layers of MnO_x of various sizes.

Thus, modification of ceria-silica composite systems with copper led to formation of easily reducible highly dispersed copper oxide species with the superior catalytic properties, especially in contact with CeO_2. A detailed analysis of catalysts by XPS, Raman spectroscopy, EPR, FTIR of adsorbed CO, and TEM confirmed the conclusions made on the basis of TPR-H_2 data. Long-term catalytic tests with H_2O and CO_2-containing feed mixtures proved high stability of both prepared samples.

This work was supported by the Russian Foundation for Basic Research, project number 20-33-90065. The authors acknowledge support from M.V. Lomonosov Moscow State University Program of Development.

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Novel Cl-doped C_3N_4 catalysts for photocatalytic hydrogen production under visible light

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Conventional energy resources have been depleted to a great extent. It is therefore necessary to produce an alternative fuel such as hydrogen. One of the most interesting ways of hydrogen production is photocatalytic water splitting over semiconductor photocatalysts [1]. Graphitic carbon nitride is known as a promising photocatalyst due to its chemical and thermal stability, suitable positions of valence band and conduction band [2]. However, high recombination rate and low surface area restrict the potential application of this material. Hydrothermal treatment of carbon nitride may enhance the textural properties [3]. The doping of halogens such as chlorine decreases the recombination rate and increases the photocatalytic hydrogen evolution [2]. Earlier two these strategies have not been applied simultaneously. In this work we studied the usage of hydrothermal treatment and Cl-doping in one synthesis.

The photocatalysts were prepared by a two-stage technique. At the first stage, the mixture of melamine, D-glucose, and water was kept in an ultrasonic bath for 30 min. Then the mixture was autoclaved at 180 °C for 12 h. At the second stage, the as-prepared melamine and ammonium chloride was heated at 550 °C for 2 h [4]. The photocatalyst surface was modified with 1 wt. % of platinum. The obtained samples were labeled as 1% Pt/y-Cl, where y was the weight content of NH_4Cl added at the second stage.

The obtained samples were tested in alkaline solution of triethanolamine under visible light (λ = 450 nm) [4]. For pristine 1% Pt/g-C_3N_4 the catalytic activity was 276 µmol $h^{-1}g^{-1}$. The addition of 5 wt. % of ammonium chloride at the second preparation stage led to the improvement the photocatalytic activity in two times. This effect may be attributed to the changes in the electronic structure of graphitic carbon nitride. The doping by chlorine atom led to the formation of new energetic levels which enhance the charge separation and the catalytic activity. The increase in weight content of NH_4Cl to 30 wt. % led to linear growth of the hydrogen production. The further enhancement of y value was accompanied with slight decrease of the catalytic activity. The highest reaction rate was demonstrated over the 1% Pt/30-Cl sample (1332 µmol $h^{-1}g^{-1}$).

Additionally, the photoelectrochemical tests were conducted in two-electrode cell, the studied samples served as a worked electrode, Cu_2S/brass was a counter electrode, the electrolyte consisted of 1 M Na_2S_n + 0.1 M NaCl [5]. The dependence of the short-circuit current density on the content of ammonium chloride at the second preparation stage was obtained. It was the same as the dependence of the photocatalytic hydrogen production activity on the NH_4Cl amount.

To sum up, the Cl-doping of graphitic carbon nitride united with the hydrothermal treatment was a good strategy for improving the catalytic properties. By this way, the enhancement of the photocatalytic activity in 4.8 times was reached by varying of NH_4Cl amount.

This work was supported by the grant of President of Russian Federation, grant MK-2133.2022.1.3.

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Hydrogenation of abies wood ethanol-lignin with molecular hydrogen in ethanol medium with a NiCuMo/SiO_2 catalyst

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Renewable lignocellulosic biomass is an alternative to traditional petroleum feedstock in the production of various chemical products [1]. The complex composition and structure of woody biomass, consisting of three main components – cellulose, lignin and hemicelluloses [2] make it difficult to chemically process it into demanded chemical compounds.

Traditional industrial technologies are focused on processing only the cellulose component of woody biomass [2]. However, lignin is one of the main components of biomass and a potential source of valuable aromatic substances [3]. Recently, research on the production of cellulose by the method of organo-solvent pulping has intensified. In this case, organo-solvent lignins are formed, which do not contain sulfur and have an increased reactivity.

In this work, we studied the effect of the bifunctional NiCuMo/SiO_2 catalyst on the yield and composition of liquid, solid, and gaseous products of abies wood ethanol-lignin hydrogenation with hydrogen in ethanol at 250°C. We used fir wood of composition (% based on the mass of absolutely dry wood): 45.7 – cellulose; 25.3 – lignin; 17.7 – hemicelluloses; 6.2 – extractives; 0.5 – ash. The wood was crushed to particles less than 1 mm in size. Isolation of ethanol lignin according to the procedure [4]. The NiCuMo/SiO_2 catalyst was prepared by the sol-gel method [5].

During the hydrogenation of ethanol-lignin in supercritical ethanol at a temperature of 250°C in the presence of a NiCuMo/SiO_2 catalyst, fir ethanol lignin is almost completely converted into liquid and gaseous products. Compared to the non-catalytic experiment, the yield of liquid products increases from 75 to 88 wt.%.

The NiCuMo/SiO_2 catalyst increases the overall yield of gases and changes their composition compared to a non-catalytic process. A significant increase in the CO yield (from 1.3 to 4.8 wt.%) indicates an intensification of the decarbonylation reaction during lignin hydrogenolysis in the presence of a nickel-containing catalyst.

The molecular weight distribution of liquid products of non-catalytic hydrogenolysis of ethanol lignin is characterized by a low degree of polydispersity (2.51) and a weight average molecular weight Mw 1680 Da, which indicates a low degree of ethanol lignin depolymerization. The catalyst promotes an increase in the content of dimeric and monomeric compounds in liquid products while retaining some of the oligomers, which leads to an increase in polydispersity up to 2.88.

Analysis of the composition of the liquid products of the hydrogenation of fir ethanol lignin by GC-MS showed that in the process of non-catalytic hydrogenation, the total yield of phenolic derivatives is 4.5 wt.%. The bifunctional NiCuMo/SiO_2 catalyst increases the total yield of dimeric and monomeric methoxyphenols to phenols by a factor of 2 (up to 9.2 wt.%).

The obtained methoxyphenols can be used as components of epoxy resins, fuel additives, and in other areas.

The reported study was supported by Russian Science Foundation, Grant No 21-13-00250.

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Photocatalytic CO_2 reduction under UV- and visible light irradiation: the effect of CuO_x cocatalysts

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Today, humankind faces the problem of an increase in the emission of greenhouse gases, and their utilization is increasingly becoming the actual goal. Additionally, special attention is paid to utilizing the major component of greenhouse gases – CO_2 [1]. A promising approach to utilizing CO_2 is its photocatalytic conversion to more reactive substances, such as CO and CH_4. This technology allows reducing the amount of CO_2 in the atmosphere [2]. Moreover, the products of this process are organic compounds, such as methane, methanol, ethanol, and formaldehyde, which could be then converted into valuable organic components or fuels. It is worth noting that such organic compounds could be synthesized using renewable sources: light, CO_2, and water.

This research focused on a study of CuO_x influence on the action spectra of TiO_2- and g-C_3N_4-based catalysts in photocatalytic CO_2 reduction. Also, Pt cocatalyst was used for comparison of photocatalyst activity. The reduction of CO_2 was studied under irradiation of light-emitting diodes with different wavelengths in the range from 380 to 425 nm, and the catalysts were characterized by transmission electron microscopy, X-ray photoelectron spectroscopy, and UV-Vis spectroscopy.

Commercial titanium dioxide Evonik P25 was used for photocatalyst preparation. For thermal activation, TiO_2 was pre-calcined at 700 °C for 3 h. G-C_3N_4 was synthesized from melamine by heating at 600 °C for 2 h. Platinum and CuO_x were deposited on the surface of prepared photocatalysts by impregnation with H_2PtCl_6 or $Cu(NO_3)_2$ followed by reduction with a 2.5-fold excess of $NaBH_4$. The reduction of CO_2 was carried out in a batch reactor (70 mL) with a quartz window (16 cm^2) under light irradiation. 1 mL of water was added into the reactor before the reactor was purged with CO_2 (>99.94% purity) for 1 h. A kinetic experiment was carried out for 24 h. Gas probe was taken using a gas syringe (500 μL) and analyzed with a gas chromatograph "GH-1000" (Chromos, Russia) equipped with the flame ionization detector and thermal conductivity detector to identify the products of CO_2 reduction and H_2, respectively.

It has been shown by XPS and XANES, the copper presents in various states (Cu^0, Cu^{+1}, Cu^{+2}), and the CuO_x/TiO_2 700 (CuO_x is deposited on the surface of TiO_2 calcined at 700 °C) sample contained less Cu^{2+} than Cu/TiO_2, but this sample had a uniform distribution of cocatalyst, which is beneficial for the CH_4 production under irradiation of visible light. This photocatalyst demonstrated fairly good stability over 120 h of CO_2 reduction. For both materials – TiO_2 and g-C_3N_4 – the substitution Pt with Cu allow one to increase the photocatalyst activity under visible light irradiation. At 425 nm, the Cu/TiO_2 700 demonstrated a maximum CO_2 reduction rate of 11 μmol h^{-1} g^{-1}, which is higher than activity of platinized sample by a factor of 2. Under UV light, Pt-containing photocatalysts demonstrate higher CO_2 reduction rates. It is caused by enhanced adsorption of Cu-containing samples due to intrinsic adsorption of copper oxides and uniform distribution of particles over the surface of calcined TiO_2, as is shown by HR TEM.

This study was supported by Russian Science Foundation (Grant #21-73-10235).

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One-pot 5-HMF hydroamination with nitro aromatic compounds over mineral-like copper catalyst

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Catalytic conversion of 5-hydroxymethylfurfurol (5-HMF), one of the most important platform chemicals obtained from plant biomass, represents a promising strategy for the implementation of "green" processes in the modern organic chemistry. Among different ways of catalytic valorization of 5-HMF, selective synthesis of amines through reductive amination is still not studied well. Amine derivatives of 5-HMF are valuable building blocks in the synthesis of drugs, polymers, agrochemicals [1]. 5-HMF can be converted to both primary and secondary amines through the hydroamination reaction. To date, the examples of the synthesis of secondary amines from 5-HMF are restricted by one- or two-stage processes, in which 5-HMF react with the amine with subsequent hydrogenation of the obtained intermediate imine to the corresponding secondary amine [2–3]. Two different catalytic systems are usually used for this reaction, while the first step can proceed without any catalyst [4]. However, from the modern industrial chemistry perspective, it is more attractive to use readily available nitro compounds as a precursor of primary amine, which then react with 5-HMF in "one-pot" regime with the formation of a target secondary amine. Although there are examples of the reductive amination of aldehydes and ketones with nitro compounds both on supported Pd, Pt, Au catalysts and over the catalytic systems based on non-noble metals (Co, Cu, Ni) [5], "one-pot" reductive amination of 5-HMF with nitro compounds has not been reported yet.

Recently, we have shown that synthetic Cu phyllosilicate materials are active in hydrogenation of nitro aromatic compounds [6]. In this work we have synthesized a novel catalyst based on copper phyllosilicate structure and doped with CeO_2 for the one-pot hydroamination of 5-HMF with nitro-aromatic compounds. It was shown that corresponding secondary amines can be obtained with high yields (up to 90%) over the obtained catalysts under relatively mild conditions (150 °C, $P(H_2) = 15$ atm). The catalysts can be recycled for at least 4 runs with no loss of activity. This is the first example of a direct 5-HMF amination with nitro compounds over the easily available non-noble heterogeneous catalysts; this finding has a high perspective for the industrial application as a "green" and atom-economy process for the valorization of bio-derived 5-HMF to the highly valuable amines.

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Magnification of the activity of highly defective copper-doped titanium dioxide at photocatalytic hydrogen generation

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The search for alternative "green" fuel sources for safe life is an actual task for scientists. To solve the problem of the future energy and environmental approach can be the use of a clean, safe, non-toxic fuel, such as hydrogen, obtained by photoconversion of the abundance of solar energy into chemical [1]. An efficient hydrogen evolution reaction (HER) requires the introduction of active catalysts into the system. Titanium dioxide remains one of the most promising photocatalysts. Pure TiO_2, in addition to the well-known advantages, has a number of disadvantages: insufficient charge separation, low efficiency of visible radiation, etc. The synthesis of new materials that will combine the advantages of TiO_2 while minimizing its disadvantages will make it possible to increase the efficiency of the catalyst. For example, by doping it, affecting the defectiveness, energy structure and conductivity, or by creating composite materials with other semiconductors, providing a second type heterojunction or a Z-scheme. Among the promising materials that allow this was done are copper and its oxides [2].

To solve the problem of synthesizing hybrid catalysts based on TiO_2 with improved photocatalytic (PC) characteristics, the method of pulsed laser ablation (PLA) was chosen. The method of preparation catalysts was similar to the technique described in Ref. [3]. At the beginning, individual colloids were obtained by PLA of titanium and copper metal targets in distilled water. The freshly prepared colloids were then mixed and processed in an ultrasonic bath. Next, the solutions were dried in air at a temperature of 60°C, and the resulting powders were annealed at 400°C. A series with a mass ratio of 0.25–50 wt.% CuO to TiO_2 was synthesized. The physicochemical characteristics of the prepared samples were studied by XRD, UV-vis diffuse reflectance and IR-spectroscopy, zeta-potential and other methods. The PC properties of Cu-TiO_2 nanoparticles (NPs) were studied in the decomposition reaction of the model organic dye Rhodamine B and in the process of hydrogen generation in the presence of a sacrificial agent, glycerol. The dye decomposition was monitored photometrically using a Cary 100SCAN spectrophotometer, and hydrogen evolution was monitored using a Chromatec Crystal 5000 gas chromatograph with a thermal conductivity detector (TCD, katharometer). The radiation sources were LEDs with wavelengths of 375 nm and 470 nm.

It was found that in samples with a Cu content of 5% or less, the formation of a separate phase of copper or its oxides does not occur. In this case, the conductivity type of the material and the zeta potential change, which probably indicates that TiO_2 is doped with copper. At a higher copper concentration, a CuO/TiO_2 composite is formed.

Cu-TiO_2 samples showed high PC activity both in the decomposition of the dye and in HER, especially when irradiated with visible light. The optimal concentration of the dopant was about 0.5 wt.%. Composite particles with the CuO/TiO_2 heterostructure, which are formed upon the addition of high concentrations of copper, lead to a decrease in the PC activity compared to TiO_2 NPs, since a not optimal heterostructure of the first type is presumably formed.

This work was supported by the Russian Science Foundation (project 19-73-30026).

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Effect of the second metal addition on the behavior of Pd-containing polymeric catalysts in Suzuki cross-coupling

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Last decade the development of bimetallic ligand-less systems including Au-Pd ones causes great interest [1–3]. Such structures exhibit higher activity, selectivity and stability as compared to monometallic analogues in Suzuki cross-coupling. Bimetallic Cu-Pd catalysts are also able to increase the efficiency of cross-coupling processes. However, there is a limited number of studies [4] devoted to the use of copper-containing catalytic systems.

In the framework of this study, mono- (Pd) and bimetallic (Au-Pd, Cu-Pd, Zn-Pd) ligand-less catalysts based on hyper-cross-linked polystyrene of MN100 type were synthesized using palladium acetate as a precursor. Pd content was 1 wt.% in all the catalysts. Content of the second metal (Au, Cu or Zn) was 2 wt.%. Synthesized mono- and bimetallic samples were tested in Suzuki cross-coupling reaction between 4-bromoanisole (4-BrAn, 1 mmol) and phenylboronic acid (PBA, 2.5-fold molar excess) while using 0.28 mol.% of Pd and NaOH (3-fold molar excess) as a base. The reaction was carried out in a batch mode under air. All the experiments were carried out using EtOH-H_2O mixture (4:1) as a solvent, which ensured that the system remained homogeneous in the whole range of the selected concentrations of both reactants (4-BrAn, PBA, and NaOH) and products.

It was shown that the introduction of Au into the catalyst composition results in noticeable increase of activity, regardless of initial oxidation state of palladium (Pd(II) or Pd(0)). In the case of unreduced samples, the addition of Cu led to an increase in catalytic activity. After the reduction in a hydrogen flow at 300 °C the activity of Cu-Pd sample decreased and became comparable to reduced monometallic Pd catalyst. On the contrary, the introduction of Zn into the catalyst composition had positive effect in the case of preliminarily reduced Zn-Pd catalyst. It is noteworthy that only the addition of copper allowed increasing the selectivity with respect to cross-coupling product up to 92–93% at 100% 4-BrAn conversion, while for all other samples the selectivity was about 89%.

For the most active bimetallic sample (preliminarily reduced Au-Pd/MN100), the effect of the reaction temperature and PBA loading was studied. Variation of the temperature in the range of 40–60 °C allowed calculating the apparent activation energy (128 kJ/mol). With a further increase in temperature from 60°C up to 70°C the observed initial reaction rate remained virtually unchanged. This may indicate the transition of the reaction to the diffusion region. However, the increase of temperature led to the increase of selectivity with respect to cross-coupling product up to 96–97%. The decrease in the amount of PBA from 2.5 mmol to 1.5 mmol was found to has practically no effect on the cross-coupling rate. The use of 1.5-fold excess of PBA in the case of reduced Au-Pd/MN100 was sufficient to reach 100% conversion of 4-BrAn for the reaction time of 15 min, which makes this catalytic system promising.

This work was supported by the Russian Science Foundation, grant number 20-19-00386.

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The effect of indium oxide additives into Pd/WO_3-ZrO_2 catalysts for the isomerization of heptane

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Every year the requirements for commercial fuels become stricter. The content of sulfur and aromatic hydrocarbons, especially benzene, is severely restricted. For this reason, research and development of more modern catalysts for secondary upgrading processes is one of the actual directions of modern oil refining.

Currently the main component of motor gasoline is reformate, which contains up to 80 wt.% of aromatic hydrocarbons. Considering this fact, there is a need to reduce the fraction of reformate in commercial fuels by involving more environmentally benign compounds.

One of the perspective solutions to this problem is an isomerization process for the C_7 fraction, which is usually sent to the reforming process. This would significantly reduce the proportion of reformate and, at the same time, increase the proportion of isomerate. In its turn, isomerate is a high-octane and environmentally friendly component of motor fuels.

Systems based on WO_3-ZrO_2 are the most perspective catalysts for this process, which possess high activity and selectivity [1–4]. The authors [5–6] prove that the properties of these catalysts can be regulated by introducing modifiers, including indium oxide.

On this basis, the purpose of this work is to investigate the effect of addition of indium oxide to tungstated zirconia catalysts on heptane isomerization. The amount of indium oxide in the catalysts was varied from 0.5 to 3 wt.%, WO_3 content was 25 wt.%. Palladium was used as the metallic component and its content was 0.3 wt.%. The calcination temperature of the acid component was 950 °C.

The obtained Pd/In_2O_3-WO_3-ZrO_2 (Pd/IWZ) catalysts were tested in heptane isomerization reaction. Reaction conditions: T=110–220°C; P=1,5 MPa; H_2/Heptane = 3 (mol.); LHSV = 1 h^{-1}.

It was shown that the introduction of In_2O_3 into the catalysts in an amount of 0.5–1.5 wt.% leads to an increase of their activity: a shift of the temperature conversion dependences by 40–60 °C towards lower temperatures is observed. The lower reaction temperature by 40–60 °C due to the addition of indium oxide in Pd/WO_3-ZrO_2 catalysts will provide the decreasing of energy and technological costs of the isomerization process.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the governmental order for Boreskov Institute of Catalysis (project AAAA-A21-121011890074-4).

The studies were carried out using facilities of the shared research center «National center of investigation of catalysts» at Boreskov Institute of Catalysis.

The authors thank G.G. Savel'eva for assistance in the study.

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New catalysts for the furfural conversion based on MAl-layered hydroxides (M=Mg, Ca, Co, Cu)

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Furfural derived from renewable raw materials is platform molecule that allows the synthesis of a number of industrially valuable products. In this regard, directions that allow the involvement of furfural in various chemical reactions are relevant. Such important routes are the reactions of the furfural hydrogenation and aldol condensation of furfural with ketones. The catalysts used in these processes have significant disadvantages. This initiated the development of new catalytic systems.

This work aimed to study the effect of the nature of metals and their ratios in the catalysts based on MAl-layered hydroxides (M=Mg, Ca, Co, Cu) on their physicochemical and catalytic properties in the aqua phase furfural hydrogenation and aldol condensation of furfural with acetone.

The preparation conditions of LH with different cationic composition were optimized. The study of the phase composition of the materials obtained by XRD confirmed the presence of one hydralcite-like phase in the samples. The formation of this phase was also confirmed by the thermal analysis data. The thermograms of the samples showed mass loss peaks typical of hydrotalcite at low and high temperatures, the position and intensity of which were determined by the cationic composition of the starting materials. The reduction process of Co and Cu from the oxide phase was studied for Co- and Cu-containing LH (after calcination). It was shown that the decrease in the maximum reduction temperature occurred with increasing of the Cu content. Therefore, this suggests the formation of bimetallic CoCu particles in the composition of CoCuAl oxides, which contributed to an easier reduction of metals.

It was shown that catalysts based on the Mg(Ca)Al-LH have a high activity in the aldol condensation of furfural with acetone. The total furfural conversion was achieved for all study samples. An increase in the M^{2+}/Al ratio, as well as the replacement of Mg by Ca in the composition of the MAl catalyst, contributed to an increase in the reaction rate. Thus, the complete conversion for the MgAl sample (Mg/Al=2) was achieved after 150 minutes of reaction, while for the CaAl sample (Ca/Al=2) - after 90 minutes. At the same time, Ca-containing catalysts are characterized by high (>99%) selectivity for the formation of furfurylideneacetone.

Dependence was established between the composition of LH-based CoCu catalysts (M^{2+}/Al, Co/(Co+Cu), their pretreatment conditions (reduction temperature), reaction conditions, and the catalytic activity of the samples in the hydrogenation of furfural. It was found that the use of a high reduction temperature (800 °C) decreases in the activity of Cu-containing catalysts. This, apparently, is explained by the sintering of particles, the enlargement of their sizes, and the decrease in dispersion. The CoAl catalysts showed high activity in the reaction even under severe treatment conditions (furfural conversion >90%) with high selectivity of furfuryl alcohol formation (>99%) under mild reaction conditions (T = 90 °C, P = 2 MPa).

We express our gratitude to Bezzubov E.A. and Lysova E.I. for help with the experiments.

The study was funded by the Russian Science Foundation grant № 22-23-20040, https://rscf.ru/en/project/22-23-20040/.

Selective hydrogenation of levulinic acid to γ-valerolactone over NiMo-SiO$_2$ catalyst

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γ-Valerolactone (GVL) is a platform molecule fabricated from lignocellulosic biomass via cascade of catalytic reactions, which draws much attention due to its low toxicity and physicochemical stability. GVL has high boiling (207°C) and low melting point (31 °C). It does not decompose or degrade even in the presence of water or oxygen. GVL is a promising substrate for production of various value-added chemicals, biopolymers, biofuels and a "green" solvent and also finds its application in the food and pharmaceutical industries and can be used as a fuel additive. Both cellulose and hemicelluloses can be used as a feedstock for GVL production, which makes the process economics more attractive [1].

GVL is obtained by catalytic hydrogenation of levulinic acid (LA) and its esters – alkyl levulinates (AL) [1]. Currently, the base metal catalysts are receiving more and more attention, due to their better availability compared to platinum group metals [2]. Ni-based catalysts demonstrate significant efficiency in the hydrogenation of LA and AL to GVL, but often deactivated during the process, due to intense leaching and sintering of the active component. There are methods to stabilize Ni including the use of organic solvent or adding metal promoters, such as Mo.

This work aims at the development of solid bimetallic NiMo-containing catalysts for the LA to GVL hydrogenation including their characterization and activity testing. The series of Ni_xMo_y-SiO$_2$ catalyst prepared by the sol-gel method (SiO$_2$ acts as a stabilizing agent) [3] was tested in the reaction of direct hydrogenation of LA to GVL in an aqueous medium in the temperature range of 120–200 °C and 4 MPa H$_2$. It was found the rate of LA conversion was not significantly affected by the reaction temperature drop from 200 °C to 160 °C, but a positive effect on the selectivity of the process to GVL was observed; the monometallic Ni-SiO$_2$ provided quantitative yield within 105 minutes of the reaction. The higher yield at lower temperature can be explained by the absence of GVL conversion to 2-methyltetrahydrofuran and 1,4-pentanediol [4], which occurs under more severe conditions. At the temperature as low as 120 °C, complete conversion of the substrate was still achieved, as well as quantitative GVL yield. The addition of Mo, which in some cases makes it possible to increase the activity of Ni-containing catalysts, in the case of hydrogenation of LA in GVL, reduces the rate of substrate conversion and on the selectivity of the process with respect to GVL leading to significant yield drop up to 64 mol.%.

This work was supported by RFBR Grant 20-03-00636.

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Graphene oxide modified with Ag and CeO_2 nanoparticles as a catalyst for catalytic and light-induced nitroarenes reduction

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Nowadays, the global chemical society is taking a course to develop current chemical industry to addresses the challenges in material and technology design for both energy-efficient manufacturing and environment protection. The Ag-based catalysts are in the focus of green chemistry as advantageous systems due to relatively low cost, low-temperature activity, nontoxicity, and facile preparation and modification procedures [1]. Moreover, being a plasmonic metal, nanosized silver is attractive for the surface plasmon resonance-induced photocatalytic processes under visible light irradiation [2]. The CeO_2 incorporation into Ag-containing catalysts provides the enhancement of the catalytic activity due to the metal-support interaction resulting in the interfacial charge transfer and synergistic action of the metal and oxide active sites [3, 4]. Graphene, a two-dimensional carbon nanomaterial, and its derivatives (e.g., graphene oxide (GO), reduced graphene oxide (RGO)) are considered promising environmentally benign adsorbents and catalyst supports. In addition, unique electroconductivity and synergy to metals and semiconductors allows utilizing this material as an active support in photocatalysis [5]. This work aims to synthesize the Ag-CeO_2/GO system and study its catalytic and photocatalytic activity in the 4-nitrophenol (4-NP) reduction into 4-aminophenol (4-AP) at room temperature and ambient pressure.

The graphene oxide was synthesized according to the modified Hummers' method [6]. Silver- and/or ceria-containing catalysts (Ag/GO, CeO_2/GO, Ag-CeO_2/GO) were synthesized by the deposition-precipitation technique. The synthesized samples were characterized by a set of physical-chemical methods: XRD, TGA, UV-visible spectroscopy, etc. Catalytic activity of the samples was tested in 4-NP reduction into 4-AP by sodium borohydride ($NaBH_4$) as a reducing agent at room temperature and atmospheric pressure in water medium. Photocatalytic activity was estimated in 4-NP reduction into 4-AP in presence of hole scavengers (alcohols, Na_2SO_3) under UV-visible light source at room temperature.

According to the TGA results, the synthesized support decomposes through two characteristic steps at 200 °C (decarboxylation) and 600 °C (combustion) in the oxidizing medium, which indicates the graphene oxide structure. The XRD data also indicate the GO formation by the diffraction peak at $2\theta \approx 13^o$ that is attributed to (002) plane of the hexagonal GO lattice. The average size of Ag and CeO_2 nanoparticles is about 20 nm in the Ag- and/or CeO_2-containing catalysts. The UV-visible spectra for suspension of catalysts indicate reduction of catalysts in the reducing medium and the evolution of SPR band of metallic Ag nanoparticles. The Ag-CeO_2/GO catalyst shows the highest both catalytic and photocatalytic activity and stability in the synthesized catalysts series.

To sum up, the considered synthesis technique allows preparing the Ag-CeO_2/GO catalysts that are advantageous and environmentally benign systems for both catalytic and photocatalytic processes such as nitroarenes reduction under mild conditions.

This work was supported by the Grant of the President of the Russian Federation (grant № MK-460.2021.1.3).

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Effect of support structure on the activity of Cr- and Ga-containing catalysts in the reaction of propane dehydrogenation with the participation of CO_2

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Utilization of CO_2 by its conversion into valuable products and involvement in chemical reactions is one of the most important and urgent problems of catalysis. Therefore, the use of CO_2 as a mild oxidizing agent in the reaction of propane dehydrogenation to propylene is a promising method for its utilization and use [1]. However, CO_2 is a kinetically stable molecule, therefore, in order to carry out the reaction of propane dehydrogenation with the participation of CO_2, a catalyst capable of activating it is required. Supported chromium and gallium oxide catalytic systems showed the highest activity in this process, the activity of which depends on the physical and chemical properties of the support [2–4].

To conduct a comparative study of the activity of Cr- and Ga-containing catalytic systems in the reaction of propane dehydrogenation with the participation of CO_2, a series of catalysts containing 5 wt.% Cr and 7 wt.% Ga and deposited on SiO_2 with different texture characteristics: S_{BET} (SiO_2-A)=747 m^2/g, S_{BET} (SiO_2-D)=181 m^2/g, S_{BET} (SiO_2-K)=241 m^2/g.

The acid-base properties of supports and catalysts were studied by diffuse reflectance IR spectroscopy. Carriers according to the strength of Brönsted acid sites (BAS) are arranged in a row: SiO_2-A > SiO_2-K > SiO_2-D. After the deposition of gallium oxide on the support surface, the order in terms of the BAS strength of the catalysts is retained, while the Cr-containing samples are in the following order in terms of the BAS strength: 5Cr/SiO_2-K > 5Cr/SiO_2-D > 5Cr/SiO_2-A.

The catalytic systems were studied in the reaction of propane dehydrogenation in the presence of CO_2 in a flow catalytic unit at atmospheric pressure and in the temperature range of 550–750 °C.

The reaction of propane dehydrogenation with the participation of CO_2 on all catalytic systems proceeds with the formation of the target product - propylene, and by-products such as methane, ethane and ethylene. For all catalytic systems, an increase in propane conversion and a slight decrease in propylene selectivity are observed with increasing temperature. The initial conversion of propane on Cr- and Ga-containing catalysts decreases in the series SiO_2-A>SiO_2-K>SiO_2-D.

The highest propane conversion (68%) at 700 °C is observed for the 5Cr/SiO_2-A sample, while the highest selectivity (84%) is observed for the 7Ga/SiO_2-A sample at 650 °C.

The study was carried out at the expense of a grant Russian Science Foundation (Project № 20-73-10106).

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Colloidal Pd-Au catalysts for 5-HMF oxidation: Effect of particle composition

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Currently, the application of biomass becomes promising due to the high renewability of the feed as well as an opportunity to synthesize a wide spectrum of valuable compounds including useful side products such as 5-hydroxymethylfurfural (HMF) formed during the refining [1]. The HMF is a multifunctional platform molecule used to synthesize various important materials ranging from healthcare products to polymers. Among others, the 2,5-furandicarboxylic acid (FDCA) is an important product of the HMF oxidation serving as an alternative source for polymer production and other syntheses [2].

Various catalytic systems were proposed for the HMF selective oxidation that influenced the selectivity towards the desired products [3], with the supported noble metals (Au, Pd, Pt, Ag, etc.) being the most abundant ones. To achieve better catalytic performance, different bimetal structures can be used [4]. However, more detailed understanding of the bimetallic catalysts is required including model unsupported systems.

The pulsed laser ablation (PLA) in liquids attracts attention as an alternative approach to obtain the high-purity colloidal particles in contrast to chemical methods that is characterized by the presence of various substances in the resulting suspensions affecting the properties of colloidal particles and limiting their applications.

This work is devoted to the study of effect of composition of colloidal Pd-Au catalysts prepared by the PLA in HMF oxidation.

The Pd and Au dispersions were prepared by the PLA of Pd and Au targets, respectively, in distilled water using Nd:YAG laser (1064 nm, 20 Hz, 7 ns). The xAu100-xPd (x = 20, 40, 60, and 80 wt.%) dispersions were obtained by the PLA of mixtures of Pd and Au dispersions. The obtained samples were characterized by electrophoretic light scattering, UV-vis spectroscopy, and SAED. The catalytic oxidation of HMF were carried out in the Parr 5500 HR compact reactor under 5 atm O_2 and at 80ºC for 22 h. The composition of catalytic mixture was analyzed by HPLC.

The UV-vis spectroscopy and SAED data clearly confirmed the formation of bimetallic AuPd particles in the xAu100-xPd dispersions. Thus, the characteristic absorption peak of Au NPs surface plasmon resonance (SPR Au) at 523 nm, which is present in the spectrum for the Au dispersion, disappears in the absorption spectra for the xAu100-xPd dispersions. The analysis of SAED data for Au, Pd and 60Au40Pd samples revealed that a lattice parameter *a* for AuPd particles (4.00 Å) lies between those of Au (4.07 Å) and Pd (3.95 Å). Besides, the electrokinetic characteristics of the dispersions indicate the changes of the surface properties for bimetallic AuPd samples in contrast with those of based on Au or Pd.

The results for catalytic HMF oxidation over the obtained samples show that the formation of bimetallic AuPd particles ensures higher activity and selectivity towards FDCA for all colloidal xAu100-xPd catalysts as compared with the Pd and Au samples. The best catalytic performance was observed for 60Au40Pd sample showing 40 mol.% FDCA yield against 7 and 6 mol.% FDCA yield for Au and Pd samples, respectively. These results indicate a synergistic effect in bimetallic AuPd NPs, with their composition strongly affecting the catalytic properties.

This work was supported by the Russian Science Foundation, grant No. 19-73-30026.

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Influence of mass transfer on the process of lignins catalytic oxidation into vanillin and pulp

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The possibilities of renewable plant raw materials processing into products of fine chemicals are actively studied nowadays and are focused on replacement of fossil raw materials. Lignins are inexhaustible sources for the production of aromatic aldehydes, which are valuable raw materials for the pharmaceutical, food and perfume industries. The most promising methods for vanillin and syringaldehyde production are catalytic oxidation of lignins with oxygen [1]. An effect of reagents` mass transfer intensity on the speed and selectivity of the process is a poorly studied problem of lignins catalytic oxidation [2, 3, 4]. The goal of this work is to study quantitatively the effect of mass transfer intensity on the catalytic oxidation of lignins with oxygen to aromatic aldehydes and pulp.

Catalytic oxidation was carried out in a 1 l stainless steel autoclave with stirring at a temperature of 160 °C and a partial oxygen pressure of 0.2 MPa. Gas liquid chromatography was used for analysis for vanillin and syringaldehyde.

The process of catalytic oxidation with oxygen permits to process biomass materials into aromatic aldehydes and cellulose. The latter can be converted into glucose, ethanol, levulinic acid and other valuable products using enzymatic, microbiological and chemical methods.

Influence of the mass transfer main parameters (stirring speed and reaction mass volume) on the native lignins oxidation speed was quantitatively studied for the first time. A linear relationship linking the oxidation process speed with the stirring was found, and the inclination angle tangents of these lines, tgφ, were calculated. In our opinion, the physical meaning of such parameter tgφ reflects the efficiency of stirring power using to intensify the mass transfer. Previously unknown linear relationship between tgφ and the reaction mass volume was found. The relationships obtained allow to reduce the searching complexity for optimal conditions of vanillin and syringaldehyde obtaining by oxidation of lignin-containing raw materials.

The research carried out shows that the previously determined relationship of the oxygen consumption speed on the stirring speed is reproduced switching from flax shives to pine wood.

It is shown that the relationship of tg on reaction mass volume is linear, and its extrapolation to the stirring speed close to zero value ($N = 1$) gives $tg\varphi = 0$, which corresponds to the process switching from diffusion to kinetic regime at zero volume of the reaction mass.

Comparison of the considered results with vanillin yields during nitrobenzene oxidation, as well as with the best results of oxygen oxidation under similar conditions shows that in the diffusion mode it is possible to obtain maximum vanillin yields that coincide within the accuracy of the experiment with the theoretical yield limit, i.e. with the maximum yield in the kinetic mode.

This work was supported by RSF Grant № 20-63-47109.

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Hydroisomerization of fatty acids triglycerides on sulfide zeolite-containing catalysts. Influence of the type of zeolite framework

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One of the current trends in the production of fuels is the development of technologies using biomass as a feedstock. Biofuels are a "carbon neutral" alternative to conventional fuels. Fatty acid triglycerides are promising biorenewable raw materials. After the process of hydrodeoxygenation (HDO), C_{15} - C_{18} alkanes are obtained from them. The addition of fatty acid triglycerides to the feedstock for hydrotreating diesel fractions leads to a number of positive effects, in addition to increasing "carbon neutrality": a decrease in the content of aromatic compounds, a decrease in density, an increase in the cetane number, etc. However, a significant disadvantage is the dramatic decrease of low-temperature properties due to the large amount of paraffins in the product [1].

Traditional hydrotreating catalysts are Co(Ni)Mo sulfides supported on an alumina support. One of the ways to improve the low-temperature properties of the product is to modify the catalyst by adding acidic additives that facilitate the cracking/hydroisomerization reactions. Classical acid components of hydroprocessing catalysts are zeolites - microporous aluminosilicate materials with a complex pore structure. Despite the fact that zeolite catalysts have been studied for more than half a century, the effect of the composition and structural type of zeolite on the hydroconversion of triglyceride feedstock is practically unstudied.

The purpose of this work was to study the effect of the composition, type and amount of zeolite additive on the activity of sulfide NiMo catalysts in the reactions of HDO - hydroisomerization of triglycerides of fatty acids.

Catalysts containing zeolites of type Y, Beta, MFI and MTT were studied. The obtained catalysts were studied by a wide range of physical-chemical methods: TPD, porosimetry, TEM, XPS, XRD, and FTIR of adsorbed pyridine. The catalytic activity of the catalysts was determined in the process of HDO/ hydroisomerization of rapeseed oil. The influence of technological parameters on the efficiency of the process was investigated.

It has been found that increasing the silica/aluminum ratio leads to a decrease in the proportion of cracked products and an increase in the proportion of hydroisomerization. However, catalysts based on zeolites with too high silica/aluminum ratio are less active, probably due to the low number of acid sites. Among zeolites, catalysts based on zeolite MTT and Y have the highest isomerization selectivity, while the MTT catalyst produce mainly mono-branched isomers, and the Y catalyst produce mainly multi-branched isomers. Beta and MFI zeolite-based catalysts lead predominantly to cracking products regardless of the framework composition. In general, the key to the development of the active and selective catalyst is the control of the type of zeolite and its composition.

The study was financially supported by the Russian Science Foundation (project no. 21-79-10140, https://rscf.ru/project/21-79-10140/).

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Synthesis of GTL oils on pelletized silicoalumophosphate SAPO-11 with hierarchical porous structure

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One of the most significant world scientific achievements in the field of oil and gas chemistry over the past 10 years is the development and implementation by Shell of a technology for the production of Group III+ synthetic oils from natural gas. These oils contain mainly isoparaffins in their composition, the presence of which provides higher thermal and oxidative stability, low volatility, high viscosity index and better low-temperature properties compared to group III oils obtained by hydrocracking followed by isodewaxing of petroleum feedstock. According to a number of properties, these oils are close to polyalphaolefin oils (PAO) of group IV, while they are significantly cheaper than the latter. The implementation of this technology became possible due to the use of catalysts based on zeolites with a one-dimensional channel structure with an input window size of ~5 Å, such as SAPO-11, ZSM-23, ZSM-48, MeAPO-11, etc. Among these materials, a special of interest is the SAPO-11 silicoaluminophosphate molecular sieve due to the presence of moderate acid sites, which can provide higher selectivity in the hydroisomerization of high molecular weight waxes [1].

It should be noted that in industrial catalytic processes, molecular sieves are used in the form of granules, which are obtained by forming a powdered zeolite with a binder material, such as aluminum monohydroxides, followed by drying and calcination at 500–650°C [2]. During the formation of granules, partial blocking of the pores of zeolite crystals by binder particles can occur, which will lead to a decrease in the availability of catalytically active centers, in addition, binders can increase the contribution of cracking side reactions. The solution to these problems can be the creation of a granular molecular sieve SAPO-11 with a hierarchical (micro-meso-macroporous) structure that does not contain binders.

In this work, the catalytic properties of Pt-containing (0.5 wt.%) granular SAPO-11 with a hierarchical porous structure in the hydroisomerization of GTL waxes and catalysts obtained by our own technology were studied for the first time [3, 4]. Samples of granulated SAPO-11 are characterized by specific surface S_{BET}=250–280 m^2/g, micropore volume V_{micro} = 0.08 cm^3/g, mesopore volume V_{meso} = 0.25–0.35 cm^3/g and macropore volume V_{macro} = 0.20–0.31 cm^3/g, total acidity NH_3 ~350–500 μmol/g. The hydroisomerization process was carried out in a flow reactor at 5 MPa, 300–400°C, H_2/n-paraffin-1000, 1.0–2.0 h^{-1}.

It is shown that the proposed catalytic system makes it possible to obtain GTL synthetic oils with a yield of more than 60%, corresponding to group III+.

This work was financially supported by the Ministry of Science and Higher Education of the Russian Federation, project 2019-0990.

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Photocatalytic hydrogen production on g-C_3N_4 with a low content of platinum

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The growing demand for energy, as well as the depletion of the reserves of used fuel, attracts the attention of researchers to the development of new environmentally friendly and inexpensive energy sources, for example, hydrogen production as a clean and promising fuel. One of the most urgent areas of sustainable energy development is the development of solar energy. This process is constrained by the fact that there are few catalysts that are activated under visible light and are capable of water splitting [1]. This process is hampered by the fact that there are few catalysts that are activated by visible light and are capable of water splitting. One of the interesting photocatalysts is graphite carbon nitride, which is activated by visible light and has high chemical and thermal stability, as well as high stability, which allows its surface to be modified without changing its composition and structure. But g-C_3N_4 has such significant disadvantages as fast charge recombination on the catalyst surface and a small surface area due to strong particle agglomeration during high-temperature heating of the precursor. To avoid the process of charge recombination on the surface and, consequently, to increase the rate of photocatalytic hydrogen evolution, noble metals are used as co-catalysts, and a supramolecular melamine-cyanuric acid complex has recently been proposed to obtain g-C_3N_4 with improved textural characteristics [2]. It has also recently been shown that the use of labile platinum nitratocomplexes can significantly increase the activity of photocatalysts compared to the traditional deposition of platinum from H_2PtCl_6 [3, 4].

In the present work, g-C_3N_4 was obtained by thermolysis of a supramolecular associate melamine-cyanuric acid (MCA) prepared as follows: melamine and cyanuric acid were mixed in distilled water, after which the suspension was stirred for 12 h at 90 °C. The resulting material was then calcined in an oven to 550 °C at a rate of 1 °C/min for 1 h. The platinum deposition of the appropriate content (0.01, 0.05, 0.1, 0.5 wt. %) proceeded as follows: a certain aliquot of $(Me_4N)_2[Pt_2(\mu\text{-}OH)_2(NO_3)_8]$ acetone solution was added to a suspension of g-C_3N_4 in acetone, and the mixture was stirred for 12 h. Then the resulting materials were calcined in a hydrogen atmosphere at 400 °C at a rate of 10 °C/min for 1 h. The photocatalytic hydrogen evolution was measured in an aqueous-alkaline solution of triethanolamine (TEOA – 10 vol. %, 0.1 M NaOH) under visible light irradiation ($\lambda = 425$ nm).

These approaches to the synthesis of photocatalysts based on graphitic carbon nitride made it possible to significantly increase the surface area; for $Pt_{0.5}$/g-C_3N_4, it was 289 m^2/g. The use of nitratocomplexes made it possible to obtain a uniform distribution of Pt onto the surface of g-C_3N_4, and hydrogen treatment not only provides a tight contact between g-C_3N_4 and Pt nanoparticles being formed, but also creates a more developed system of pores in g-C_3N_4. As a result of optimization of the catalyst preparation procedure, the most active sample was $Pt_{0.5}$/g-C_3N_4 – 11400 μmol g_{cat}^{-1} h^{-1} with apparent quantum efficiency at a wavelength of 425 nm equal to 6.7 %. The photocatalysts prepared in this way showed the highest rate of hydrogen production recorded to date. It is also worth noting the reproducibility of the reaction rate for photocatalysts synthesized from a larger amount of the melamine-cyanuric acid supramolecular complex.

This work was supported by RSF, grant № 21-13-00314.

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Activity of cobalt-cerium oxide catalysts in the reaction of ethanol conversion into diethyl ether

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In order to reduce harmful emissions into the environment, a course has been taken in recent years to use renewable sources of raw materials and energy. A promising renewable source of raw materials used in industry is second-generation bioethanol. One of possible product that can be made from ethanol is diethyl ether. In this regard, in this work, we studied the reaction of the conversion of ethanol to diethyl ether in cobalt-cerium oxide catalysts.

Binary cobalt-cerium oxide catalysts were prepared by precipitation of aqueous solutions of nitrate salts of cerium and cobalt. The resulting mixture was evaporated and dried at a temperature of 100-110°C, decomposed to complete decomposition of the initial salts at a temperature of 200–250 °C and calcined at a temperature of 600 °C for 10 hours. The catalytic activity of the synthesized samples was studied in a flow-through installation with a tubular reactor in the temperature range of 150–450 °C. The volumetric feed rate was 1200 h^{-1}. The ratio of the initial reagents alcohol : nitrogen = 1:9. The analysis of raw materials and reaction products was carried out by the chromatographic method.

The performed studies have shown that the products of ethanol conversion on cobalt-cerium oxide catalysts are ethylene, acetaldehyde, and diethyl ether. For a better understanding of the mechanism of the reaction of the conversion of ethanol into diethyl ether and other reaction products, we carried out a thermodynamic calculation of the reactions occurring during the conversion of ethanol. The calculation of the change in the isobar of a chemical reaction was carried out according to the Temkin-Schwartzman equation. The calculations performed showed that the change in the enthalpy of the diethyl ether formation reaction is -24420, i.e. the reaction is exothermic, and since the reaction proceeds with an increase in the number of moles, an increase in pressure leads to a shift of the reaction to the left. The calculated Gibbs energies with increasing temperature for the reaction of formation of diethyl ether increases from -15.5 kJ at 300 K to -7.0 kJ at 600 K. This indicates that the reaction of dehydration of ethanol to diethyl ether is desirable to be carried out at low temperatures. The Gibbs energies of the remaining products, namely ethylene and acetaldehyde, decrease with increasing reaction temperature and have negative values at high temperatures, which indicates that they can proceed preferentially at higher temperatures.

We have studied the reaction of the conversion of ethanol to diethyl ether on a catalyst with the composition Co-Ce = 1–9. The study of the conversion of ethanol to diethyl ether on synthesized cobalt-cerium oxide catalysts showed that the main reaction products are diethyl ether and acetaldehyde. Also at high temperatures, the products of the destructive decomposition of ethanol (carbon dioxide and methane) are formed as by-products. The results of the study of the reaction of the conversion of ethanol to diethyl ether on the catalyst Co-Ce = 1–9 showed that the reaction of the conversion of ethanol begins at 250 °C. At this temperature, 3.6% acetaldehyde and 1.6% diethyl ether are formed. With a further increase in temperature, the yields of acetaldehyde and diethyl ether pass through a maximum. The highest yield of diethyl ether is achieved at 400 °C and is 52.7%. It was also found that the maximum conversion of ethanol is achieved at a temperature of 450 °C and is 77.4%.

Hydrogenation of arenes and their mixtures on platinum catalysts

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Hydrogenation of aromatic compounds is one of the most important reactions in the chemical industry. In addition, hydrogenation of aromatic hydrocarbons contained in motor fuel improves its quality and, as a result, reduces the release of carcinogenic substances during its combustion [1]. Cyclohexane is the product of benzene hydrogenation. It is widely used for production of caprolactam. Moreover, cyclohexane is an intermediate product of pharmaceutical substances and a common solvent in fine organic synthesis.

Catalysts based on platinum group metals deposited on various supports - simple and mixed oxides (SiO_2, Al_2O_3, aluminosilicates), carbon materials, zeolites - are widely used in hydrogenation reactions of aromatic hydrocarbons [2]. Currently, polymer sorbents based on hyper-crosslinked polystyrene have become widely used as a catalyst support [3]. The use of a polymer support makes it possible to uniformly distribute metal particles in the volume of a polymer that swells well in the reaction medium. Moreover, polymeric supports tend to ensure the stability of the nanoparticles of the active phase and prevent its aggregation.

In this work, we report the use of platinum catalysts deposited on an industrial polymer sorbent MN100 and on laboratory synthesized crosslinked aromatic matrices in the hydrogenation reaction of arenes (benzene, toluene, benzene toluene mixture). We tested catalytic systems of 1% Pt/MN100, 1% Pt/C-2, 1% Pt/C-3, 1% Pt/C-4, preliminarily reduced with hydrogen for 3 hours at 300 °C, in the hydrogenation reaction of various substrates at 230°C and $P(H_2)$ 50 atm for 2 hours. The maximum hydrogenation rate for both benzene and toluene as well as their mixtures is observed for the 1% Pt/C4 system. The reaction rates were found to be 37.9 mol(Benzene)/(mol(Pt)*l*s) and 19.4 mol(Toluene)/(mol(Pt)*l*s) respectively. Moreover, the rate of hydrogenation of benzene is higher than the rate of hydrogenation of toluene. The selectivity for cyclohexane and methylcyclohexane were 100% in the presence of the 1% Pt/C4 catalyst. It is noteworthy that the activity of a platinum catalyst on a laboratory synthesized matrix is higher than that for platinum catalyst on an industrial sorbent. Thus, a catalyst based on a laboratory synthesized matrix can be used in industry for selective hydrogenation of benzene in its mixture with toluene.

In addition, the catalytic systems were analyzed by the following methods: IR spectroscopy, TGA. IR spectroscopy has shown that the catalytic matrix remains unchanged after the reaction, but partially retains the reaction product. Thermogravimetric analysis of platinum catalysts is carried out to determine the temperature stability of catalytic systems and the drying temperature of catalytic systems after catalytic tests.

This work was supported by RSF, grant number 20-19-00386.

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Production of biogenic formic acid by hydrolysis-oxidation of plant biomass and its main components in the presence of solid Mo-V-P HPA catalysts

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The extension of environmental problems such as the greenhouse effect and climate changes require a reduction of consumption of fossil hydrocarbons and utilization of new, environmentally friendly energy sources. In this regard, the use of hydrogen as a fuel is a promising area of research in the field of low-carbon energy. However, the complexity and high cost of the production and transportation of H_2 reduces its profitability as a commercial product [1]. To solve these disadvantages, the use of H_2 donor substances seems to be very perspective. For example, formic acid (FA) containing up to 53 g of hydrogen per liter of FA can be proposed as a perspective H_2 source. Using FA has a lot of advantages such as the possibility of obtaining the target product from plant biomass via a one-pot process in the presence of "green" heteropoly acid (HPA) bifunctional catalysts (OxFA process) [2]. This process takes place in air or oxygen environment and in water as an ecologically clean solvent. No hazardous byproducts derived during the OxFA processing biomass to FA.

The aim of the work is to study the process of hydrolysis-oxidation of plant biomass and its main components to FA in the presence of solid Mo-V-P HPA catalysts.

Cesium salts of HPA were synthesized via two stage technique. The amount of cesium and vanadium in the composition were varied [3]. The prepared catalysts were studied by a number of physicochemical methods (IR-spectroscopy, XRF, N_2 adsorption, pH_{zero}).

The synthesized catalytic systems were tested in the process of hydrolysis-oxidation of mechanically activated microcrystalline cellulose. The main product in the aqueous phase was FA. The yield of target product varied from 23 mol.% to 45 mol.%. The highest yield of FA is achieved in the presence of a catalyst with the composition $Cs_{3.5}H_{7.5}PMo_4V_8O_{40}$. An increase in the number of protons and vanadium in the structure of the catalyst is shown to rise the activity of the catalytic system.

The most perspective catalyst was used to optimize the process conditions. The following parameters were investigated: reaction temperature (160–180ºC), air mixture pressure (5–50 atm) and catalyst/substrate ratio (1/1(16)). The optimal process conditions were temperature – 170ºC, air mixture pressure – 20 atm, catalyst/substrate ratio – 1/2. Optimization of conditions increased the yield of FA from 45 mol.% to 50 mol.%.

Under optimized conditions, in the presence of $Cs_{3.5}H_{7.5}PMo_4V_8O_{40}$ catalyst, the conversion of plant biomass and its main components into FA was studied. Cellulose derived from oat husk, xylan and arabinogalactan hemicelluloses, organosolve lignin obtained from birch wood, miscathus, oat husk, birch and aspen wood chips were treated in the process under study. Generally, yields of FA derived from plant biomass and its components were in the range of 32–70 wt.%. The highest yields of FA equal to 70 wt.% were achieved during transformation of microcrystalline cellulose and arabinogalactan in 5 and 1 hour of reaction, respectively.

This work was supported by the Russian Science Foundation (pr. 17-73-30032).

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Environmentally friendly hydrolysis-dehydration of oat husk and its main components into 5-hydrohymethylfurfural and furfural in the presence of solid and soluble acid catalysts

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Research field for obtaining valuable chemicals from plant biomass which are environmentally friendly and renewable raw materials has a high degree of relevance. For the effective implementation of the processes, it is necessary to develop effective catalysts for these transformation as well as to reveal the optimum reaction conditions and requirements for the composition and quality of plant materials.

The mail goal of the work is producing of 5-hydroxymethylfurfural (5-HMF) and furfural from oat husk agricultural waste. The target compounds are perspective intermediates for chemical production of polymers and octane boosters (as additives for motor fuel). Oat husk are characterized by high availability, low cost, ease of obtaining, transportation and storage.

In this work, two types of catalysts were used: 1) zirconium dioxide prepared by microwave treatment of zirconium nitrate (P = 50–1000 W, T = 320–890 °C, t = 7–40 min, samples ZrO_2-W) and 2) carbon material Sibunit-4 oxidized by wet air (T = 450 °C, t = 4 h, the sample S-4-Ox-450). Pure iron phosphate $FePO_4$ was also applied in the process as catalyst.

The catalysts were investigated by low-temperature nitrogen adsorption (S_{BET} = 18-180 m^2/g), and XRD. ZrO_2-W samples contain monoclinic and tetragonal phases, as well as ZrO_2-W-N-5 sample is X-ray amorphous. pH suspension of the catalysts was also studied: ZrO_2-W (2.2–6.6), Sib-4-Ox-450 (5.0) and $FePO_4$ (3.9). The composition of oat husk was investigated by various methods. The substrate consisted of cellulose (44 %), hemicelluloses (34 %), lignin (22 %), ash content (6%), extractives (0.8 %). The moisture was 5.5 %. To derive cellulose and hemicelluloses from the biomass oat husk under goes oxidative delignification [1]. The optimal conditions of biomass pretreatment were revealed: T – 100 °C, solid/liquid ratio – 1/26, concentration of H_2O_2 and CH_3COOH – 6 and 25 wt.% respectively, oat husk activation time – 30 min. Optimization of delignification conditions let one to reduce the content of lignin in seven times from 22 to 3%.

The effectiveness of the solid catalysts of ZrO_2, S-4-Ox-450, $FePO_4$ and soluble catalytic systems of hydrochloric, sulfuric, acetic and formic acids was investigated in the process of hydrolysis-dehydration into 5-HMF and furfural of microcrystalline cellulose, cellulose and hemicelluloses derived from oat husk, and untreated oat husk. Among solid acid catalysts, the ZrO_2-W-N-5 sample is the most promising. The high activity of the catalyst is explained by its acidity, which depends on the preparation conditions.

Optimum reaction conditions for hydrolysis-dehydration with ZrO_2-W-N-5 were revealed: ratio substrate/catalyst = 16/1, reaction temperature 190 °C. The transformation of oat husk make it possible to obtain glucose, furfural and 5-HMF with the yields of 22, 11 and 5 wt.%, respectively. Fractionation of studied biomass can improve the effectiveness of furan derivatives production. Thus, the yield of 5-HMF was 7 wt.% during the hydrolysis-dehydration of cellulose derived from husk, 18 wt.%. yield of furfural was achieved from the hemicelluloses.

This work was supported by the Russian Since Foundation Grant 22-23-01012.

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Investigation of the regenerated spent hydrotreating catalyst in the conditions of cracking of model and real oil raw materials

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One of the promising areas of processing heavy oil raw materials is the development of thermocatalytic processes using a slurry-bed reactor [1].

The main task of technologists is to select the optimal catalyst that would contribute to the favorable course of the cracking reaction, while it should be relatively cheap and have a large raw material base.

There are a sufficient number of developments using molybdenum-containing catalyst samples in the processing of heavy oil residues, which are introduced in pure form or in the form of catalyst precursors [2, 3].

This type of catalyst promotes intermolecular hydrogen transfer, contributing to the production of raw materials of an average fractional composition, which is more favorable for processing.

The available raw materials containing a molybdenum compounds are spent hydrotreating catalysts, the annual global increase of which inevitably amounts to 150-170000 [4].

The regenerated spent aluminum-cobalt-molybdenum hydrotreating catalyst used in the study contains 4.31 wt.% and 20.52 wt.% MoO_3 and has a typical porous structure, with slightly reduced values for surface area and pore volume.

Tests on the study of catalytic activity were carried out in a flow-type installation under a hydrogen pressure of 1.6 MPa in the temperature range of 400–440 °C, with an LHVS of 1–3 h^{-1}.

Under these conditions, paraffin hydrocarbons enter into cracking, isomerization and formation of aromatic hydrocarbons. With an increase in the temperature of the process, paraffin hydrocarbons are more prone to the formation of cracking products, relative to isomerization products.

Naphthenic hydrocarbons are most actively involved in dehydrogenation reactions and can act as a hydrogen donor, which indicates the possibility of carrying out intermolecular hydrogen transfer reactions on a regenerated spent catalyst for hydrotreating.

The conversion of vacuum gas oil, representing a typical high-boiling fraction, was studied in an autoclave under a hydrogen pressure of 1.6 MPa in the temperature range 450–470 °C with a catalyst consumption of 0.1 % wt., the contact time was 0.5 h.

Under optimal conditions of the thermal cracking process in the presence of a catalyst, a yield of 54.5 wt.% was obtained light petroleum products with a predominance of diesel fraction (39.4 wt.%) when compared with thermal cracking under similar conditions, the increase in light was 7.6 wt.% Given that the changes in the technology of the classical thermal process are minimal, this result is significant.

Based on the analysis of the physicochemical properties of individual fractions, all products of the process under study can be involved in processing, which allows us to conclude about the possible prospect of using a regenerated hydrotreating catalyst in industrial thermodestructive processes of processing vacuum gas oil and heavy oil residues.

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Interaction of norbornene with aromatic hydrocarbons on a zeolite catalyst

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Strained unsaturated carbocyclic hydrocarbons having a norbornene (NBD) structure are important objects of organic chemistry [1]. At the same time, NBN and some of their simplest derivatives have a reliable raw material base, since they are formed from large-tonnage products of oil or coal processing: dicyclopentadiene (DCPD), 1,3-cyclopentadiene (CPD), and structural alkenes. The production of CPD can easily be combined with the production of other products. Currently, not all CPD finds a qualified application, so the search for new promising ways to use it is very relevant. At the same time, CPD itself can already now be obtained not only during the processing of oil fractions or the technology of indirect liquefaction of coal raw materials, but also by synthesis from natural products [2].

The use of catalytic methods and approaches for NBN as substrate opens exceptional opportunities for the synthesis of hard-to-reach high-density hydrocarbons of various kinds based on it, which are the key materials for aircraft to increase payload and expand flight distance [3]. The problems of selectivity and manufacturability of these reactions are fundamentally important for their practical implementation.

It was found that during the catalytic dimerization of norbornene (NBN) using some zeolite catalyst (H-Beta and H-ZSM-12) in the medium of aromatic solvents (benzene, toluene, *ortho*-xylene, *meta*-xylene, *para*-xylene, etc.), the introduction of the NBN molecule occurs along the C–H bond of the aromatic ring to form an appropriate amount of possible substituted aromatic products linked by a C–C bond to the backbone of the NBN molecule. In other words, the use of such a heterogeneous catalyst directs the process in a completely new direction, which is not realized usually with the use of homogeneous catalytic systems. The reaction proceeds in several hours at rather low temperatures (up to 150 °C) without the use of an inert atmosphere with complete conversion of NBN and high selectivity (up to 95%) for described co-dimers. The main by-products of the reaction are tricyclo[2.2.1.0$^{2.6}$]heptane, bis-2,2'-norbornylidene dimers and NBN trimers which are already known for this type of catalyst [4].

On the basis of a complex of physicochemical, kinetic, and isotope methods, the structure of the resulting isomers has been established. Some approaches have been developed to describe the mechanism of catalyst action. The conditions for obtaining some individual isomers have been developed and optimized. New data have been obtained on the participation of a wide range of aromatic compounds with various substituents in this reaction. The possibility of controlling the directions of introduction of NBN into the aromatic ring is shown. Criteria that allow the directed selection of substrates have been defined.

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Synthesis of a multicomponent MoVTeNbBi oxide catalyst for oxidative dehydrogenation of ethane

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Oxidative dehydrogenation (ODH) of small alkanes provides an important energy-efficient route to the production of alkenes that constitute essential building blocks of the chemical industry. To date, the most effective catalysts for catalyze ethane ODH with exceptionally high selectivity to ethylene at moderate reaction temperatures are mixed bulk oxides of Mo, V, Nb, Te, arranged in an orthorhombic crystalline form, known as the M1 phase [1, 2]. This phase also plays an important role in selective formation of acrolein, acrylic acid, or acrylonitrile directly from a propane feed, instead of the more conventional propene-based processes [3]. The M1 phase oxides consist of layers of interconnected octahedral Mo and V oxo groups stacked along the [001] direction. The important feature of M1 phase is the flexibility of partial replacing molybdenum or vanadium cations that form the main framework. It is also possible to introduce additional elements into micropores located along the growth axis of the M1 phase. The possibility of modifying the catalyst by introducing additives of the fifth component in order to improve the catalytic properties is of particular interest. Despite its high activity and selectivity, quaternary MoVTeNb oxide catalysts are unstable in the reducing atmosphere due to the loss of Te, causing structural instability of the M1 phase. The bismuth introduction in the MoVTeNb catalyst leads to its incorporation into the channels of the M1 structure due to its similarity to tellurium. The addition of bismuth ensures the achievement of maximum activity and stability of the catalysts [4]. However the problem of introducing bismuth additives into the catalyst and obtaining reproducible results is noted.

In this work, the conditions of synthesis were investigated, since they are essential for obtaining an active and selective orthorhombic phase M1. Bulk MoVTeNbBi mixed oxide catalysts were obtained by slurry method [4, 5]. Steps of the synthesis included mixing of aqueous solutions of the starting components, drying of the liquid precursor, and a subsequent stepwise annealing in inert atmosphere with intermediate heat treatment in air at 310 °C. The key parameters for obtaining highly active and selective M1 phase are the content of Te and Nb, the pH of the solution, the drying time of the precursor solution, and the annealing parameters. The catalytic characteristics were evaluated in the ODH of ethane to ethylene.

The necessary amount of niobium content was determined in a range of 0.08-0.16 Nb/Mo while tellurium of 0.17-0.27 Te/Mo. The pH of the medium was varied in a range of 2.3-3.7. The multicomponent MoVTeNbBi slurry was stirred during 0-95 min before drying to evaluate sample mixing time tolerance. The optimal conditions for annealing were investigated for temperatures 530-630 °C during 1-4 hours.

To establish reproducibility 5 samples with a maximum ethylene yield of about 75% were replicated. Thus, the optimal synthesis conditions and the permissible limits for varying the conditions to obtain a reproducible catalyst have been determined.

This work was conducted within the framework of the budget project for Boreskov Institute of Catalysis (No. AAAA-A21- 121011390008-4).

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Modification of ZrO_2–SiO_2 catalysts with small amount of CrO_x for non-oxidative propane dehydrogenation

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The development of new technologies that use natural resources more efficiently and environmentally friendly is an important sustainability challenge. Unsaturated hydrocarbons are the main feedstock for a wide range of polymer materials. However, production of alkenes is not a simple task. One of the most promising methods for their production is the catalytic dehydrogenation of light paraffins, including propane. The industrial dehydrogenation catalysts usually contain Pt or CrO_x particles supported on Al_2O_3. Platinum-based catalysts are expensive and easily deactivated while high chromium content can pose a threat to human health due to the possible presence of toxic Cr^{+6} compounds [1]. ZrO_2-based catalysts modified with silica and small amount of CrO_x as an active component are promising for non-oxidative propane dehydrogenation (PDH) [2].

ZrO_2-SiO_2 and CrO_x-ZrO_2-SiO_2 catalysts were prepared by the evaporation-induced self-assembly technique using cetyltrimethylammonium bromide (CTAB) and tetraethoxysilane (TEOS) as templates. After evaporation the precursors were heated up to 600 °C (2°C/min) and calcined at this temperature initially in air for 4 h and then in a nitrogen atmosphere for 3 h. The samples were denoted as ZrSi or *y*CrZrSi (where y = 4, 6.4 or 8 wt.% is the chromium loading, assuming Cr_2O_3 stoichiometry). The (Cr+Zr)/Si molar ratio was 0.8. The catalysts were tested in PDH at 500, 550, and 600 °C on an ULCat-1 catalytic unit (UNISIT, Russia) equipped with a fixed-bed continuous-flow stainless steel reactor. 100 mg of catalyst was used in each test. Long-term stability tests were carried out at 550 °C with 200 mg of the catalyst. The feed flow composition was 40 vol.% C_3H_8 and 60 vol.% N_2 (total flow rate – 30 ml/min). The gas mixture at the output of the reactor was analyzed by GC on a Crystal-5000.2 gas chromatograph ("Chromatec", Russia) equipped with a Carboxen-1010 PLOT capillary column (30 m, id 0.32 mm, "Supelco", USA) and a thermal conductivity detector.

The 8CrSiZr catalyst showed the best catalytic efficiency at 550 and 600 ºC: the propane conversion was 6 and 8% at selectivities of respectively 90 and 80%. The lowest propane conversion was observed for 4CrZrSi. Raman spectroscopy revealed the absence of the Cr_2O_3 phase active in PDH. Both Cr^{3+} species in Cr_2O_3 and those octahedrally coordinated with oxygen were observed in highly active 8CrZrSi by Raman spectroscopy. According to the XRD data the ZrSi support presents as highly dispersed crystalline particles that favors the formation of coordinatively unsaturated zirconium cations. The latter in combination with CrO_x can form active sites effective in PDH. The catalysts were also characterized by H_2-TPR and XPS.

Long-term stability tests at 550 °C led to the deactivation of CrZrSi due to the coke formation. Based on the DSC-TG data the smallest amount of coke was observed in 8CrZrSi. Regeneration of the catalysts by 30 min air treatment at 550 °C recovered both the propane conversion and propylene selectivity.

A small amount of CrO_x improves the catalytic performance of ZrSi. The catalyst activity correlates with the chromium oxidation state. The Cr-ZrO_2-SiO_2 interaction leads to the formation of additional active sites and increases the number of oxygen vacancies. The coked catalysts can be regenerated by oxidative treatment.

This work was supported by the Russian Science Foundation, project number 22-23-00445.

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Hydrolysis-oxidation of cellulose to formic acid over organic salts of Mo-V-P heteropoly acid catalysts

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Formic acid (FA) is widely used in the pharmaceutical, food, chemical industries and agriculture (fodder ensiling). In addition, FA is a promising environmentally friendly source of hydrogen (1 L FA ~ 53 g of hydrogen). Formic acid can be obtained by hydrolysis-oxidation of plant materials and / or its components using bifunctional catalysts based on heteropoly acids (HPA) [1, 2].

The aim of this work is the development of solid bifunctional catalytic systems based on Mo-V-P organic salts of HPA heteropoly acids for a process of hydrolysis-oxidation of cellulose into formic acid.

Salts based on imidazolium were obtained by slowly adding the calculated amount of $[C_xH_{2x-1}MIM]Cl$ (x – 6.10 and 16) to alcoholic solutions of $H_4PMo_{11}VO_{40}$ and $H_7PMo_8V_4O_{40}$. The obtained $[C_xH_{2x-1}MIM]$-Mo-V-P catalysts were studied using a complex of physicochemical methods (IR spectroscopy, XRD, nitrogen adsorption, pH_{PZC}). The specific surface area of catalysts was less 3 m^2/g. Surface acidity, which was evaluated by mass titration (pH_{PZC}), was in the range of 2.3–3.9. According to IR spectroscopy data, the positions of the bands related to Mo–O bonds depend on the length of the alkyl group of the $[C_xH_{2x-1}MIM]^+$ cation in the catalysts. The shift of the νs (Mo–Oc–Mo) band increases with the size of the alkyl group in the following order: $H^+ > [C_6H_{13}MIM]^+ > [C_{10}H_{23}MIM]^+ > [C_{16}H_{33}MIM]^+$.

Catalytic tests were carried out in a high pressure autoclave in the temperature range of 150–180°C, air pressure of 20–50 bar, and a substrate/catalyst weight ratio of 1/(1–0.0625). According to HPLC analysis and NMR spectroscopy, the main product is formic acid (up to 40 mol.%). Acetic and glycolic acids (up to 6 mol.%) were found as by-products. The selectivity of the formation of formic acid for water-soluble products was 89–91%. Cellulose conversion determined by analysis of the liquid fraction for total organic carbon was in the range of 27–46%. The optimal conditions for the process of hydrolysis-oxidation of cellulose in the presence of the most promising catalytic system $[C_{10}MIM]_3$-PMoV were temperature 170 °C, air pressure 50 bar, and substrate/catalyst weight ratio equal to 1/(1-0.125). The observed activation energy of the process was 136 kJ/mol. The resulting activation energy is higher than the activation energy of cellulose hydrolysis-oxidation (78 kJ/mol) in the presence of soluble HPA catalysts described in our previously published work [3].

This work was supported by Russian Foundation for Basic Research Grant № 20-03-00263.

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Conversion of dihydroxyacetone to lactic acid on a UiO-66-SO_3H catalyst

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In the modern world, in the manufacture of biodiesel from plants, the by-product is crude glycerin. Then there is the problem of its processing. In order to make the production more environmentally friendly and economically profitable, it was proposed to oxidize glycerin in an aqueous medium into valuable products, for example, lactic acid on a selective metal catalyst [1]. However, two problems appear: accumulation of the intermediate product of the reaction, dihydroxyacetone, and the need for high temperatures to achieve the greatest selectivity for lactic acid. At the same time, it is known that the conversion of dihydroxyacetone into lactic acid occurs at the Lewis and BrØnsted acidity centers contained in UiO-66 type catalysts, characterized by thermal and chemical stability, porosity. Thus, it is necessary to modify and investigate the catalytic properties of UiO-66 in the reaction of conversion of dihydroxyacetone into lactic acid in order to establish optimal conditions for its conduct.

To establish optimal reaction conditions (the effect of catalyst loading, temperature and the number of Lewis and BrØnsted acidity centers), the UiO-66 or UiO-66-SO_3H catalyst suspension and 0.3 M dihydroxyacetone aqueous solution were heated in an autoclave for 4 hours at atmospheric pressure. The resulting mixture of products was centrifuged and analyzed by high-performance liquid chromatography.

To establish the effect of temperature on the composition of the reaction mixture, catalytic experiments were carried out at temperatures from 100 to 130°C on a modified UiO-66-SO_3H catalyst. It was found that with increasing temperature, the values of both the conversion of dihydroxyacetone and the values of selectivity for lactic acid increase, which is inherent in the Cannizzaro reaction under study.

An increase in the loading of the UiO-66-SO_3H catalyst affects the conversion of dihydroxyacetone and the selectivity for lactic acid with different effects. The conversion of dihydroxyacetone at a given temperature does not depend much on the loading of the catalyst. At the same time, the selectivity for lactic acid increases by 20–30% with a doubling of the catalyst mass. These data indicate a positive effect of an increase in the number of reaction centers on the selectivity of the catalyst and the presence of side reactions and an intermediate.

To assess the effect of the presence of a catalyst and the presence of acidity centers on dihydroxyacetone conversion and lactic acid selectivity, an idle experiment without a catalyst and experiments with UiO-66 catalysts containing Lewis Zr^{4+} acidity centers and BrØnsted OH weak acidity centers, and UiO-66-SO_3H containing the same number of Lewis acidity centers, centers weak BrØnsted acidity OH and strong BrØnsted acidity centers. During the transition from the experiment without a catalyst to the experiment on UiO-66, the conversion of dihydroxyacetone and the selectivity for lactic acid increased, and in the series of UiO-66 and UiO-66-SO_3H, only the selectivity value increased. This indicates the complexity of the reaction mechanism and the presence of an intermediate, presumably methylglyoxal. Thus, for the selective conversion of dihydroxyacetone into lactic acid, both Lewis acidity centers based on Zr^{4+} and BrØnsted acid centers contained in greater quantities on the UiO-66-SO_3H catalyst than on UiO-66 are needed.

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Photocatalysts based on Bi-containing layer perovskites for dye photodegradation

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To date, the development of manufactures, in particular the textile and polygraphic, is growing rapidly. Plants release a numerous amounts of dyes in water that causes environmental pollution [1]. Photocatalysis is a perspective approach of dyes degradation since it occurs in the presence of photocatalysts and light at room temperature. Photocatalysts on basis of Bi-containing layer perovskites have advantages under other photocatalysts due to the ability to separate an electron-hole pair and absorb visible light that enhance the photocatalytic performance.

Thus, the aim of the report is to establish the influence of phase content of perovskite catalysts on their optical properties and photocatalytic activity in the reaction of Rhodamine B photodegradation.

The seria of 3 samples, namely Bi_2Si_1, $Bi_2Si_{0.5}Ti_{0.5}$, Bi_4Ti_3, was synthesized via sol-gel method. Phase composition was determined by X-ray diffraction analysis and IR-spectroscopy. Quantitative content of elements was detected with X-ray Fluorescent analysis. The value of specific surface area was measured by low temperature sorption of nitrogen. Diffuse reflectance spectroscopy was used to determine optical characteristics of the samples.

Photocatalytic activity of the samples prepared was evaluated in the reaction of Rhodamine B photodegradation, concentration of which was monitored by UV-Vis spectrophotometer.

According to XRD data, the sample Bi_4Ti_3 consists of layer $Bi_4Ti_3O_{12}$ phase, while the samples containing Si are multiphase with the prevalence of layer bismuth metasilicate phase Bi_2SiO_5. The sample Bi_2Si_1 possesses the highest value of S_{BET}, at the same time the content of silicon is in 1.5 higher than theoretically calculated one, so IR-spectroscopy was also used to confirm the phase composition of the samples. IR-spectroscopy data correlates with XRD data for each sample prepared. Additionally, in the IR-spectrum of the Bi_2Si_1 sample in region 1100–1200 cm^{-1} the vibrations of Si-O bond were detected which are characteristic for SiO_2. Obtained results specify the formation of amorphous silica due to partial hydrolysis of TEOS for Bi_2Si_1 sample.

DRS spectra demonstrate absorbance edges in region 378–395 nm for the samples containing bismuth titanates. Since the absorbance edge of Bi_2Si_1 sample is at 550 nm, the sample absorbs light in the visible area which is due to the presence of narrow-band semiconductor β-Bi_2O_3 in the composition of the photocatalyst.

Photocatalysts prepared show 100% conversion of Rhodamine B degradation via deethylation mechanism, while the reference photocatalyst α-Bi_2O_3 decomposes the dye only by 40%.

Thus, sol-gel approach allowed preparing the photocatalysts based on Bi-containing perovskite silicates and titanates which are able to decompose the Rhodamine B solution. Apart from that, the developed preparation technique let synthesize material absorbing the visible light. Though the highest photocatalytic activity was demonstrated due to separation of charge carriers inside the composite $Bi_2Si_{0.5}Ti_{0.5}$ consisted of Bi_2SiO_5, $Bi_{12}SiO_{20}$, $Bi_{12}TiO_{20}$ phases.

This work was supported by the Russian Science Foundation, grant No. 19-73-30026.

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Isomerization of n-hexane using microwave heating

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The isomerization of alkanes, such as n-hexane, is one of the best processes for achieving high quality of gasoline. It allows the formation of branched alkanes (2-methylpentane, 3-methylpentane, 2,2-dimethylbutane and 2,3-dimethylbutane), which is an interesting option for increasing the research octane number (RON), hence improving the performance of vehicle engines. This reaction also satisfies gasoline production requirements such as limited aromatic compounds, olefins, or methyl tert-butyl ether (MTBE), which is known to be a potential carcinogen [1].

The originality of this work lies in the use of microwave heating in the process of isomerization.

Recently, considerable attention has been paid to the study of the effects of microwave radiation in chemistry, in particular the effect of microwave heating on the course of catalytic reactions. Application of microwave influence on heterogeneous catalysts in the process of their preparation allows in some cases to obtain catalysts with a more uniform particle distribution, to accelerate the process of catalyst preparation, to carry out the uniform heating of the catalyst volume phase. In the case of catalysts consisting of multiple phases, the replacement of traditional heating by microwave treatment may promote the preferential formation of individual phases. Varying the radiation frequencies in some cases makes it possible to generate catalysts with a defined dispersity. When microwave activation is used in the catalytic process, a decrease in the reaction starting temperature, an increase in the activity and/or selectivity, as well as a change in the composition of the reaction products are observed in most cases [2].

Isomerization catalysts are bifunctional: dehydrogenation/hydrogenation reactions take place on metal active centers and carbon skeleton isomerization - on acidic centers.

In the current work we obtained and tested catalysts which proved themselves in isomerization process: $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ heteropoly acids (HPAs) on carbon. As a solid protonic acid, HPA can be directly used as a catalyst for various acid-catalyzed reactions. However, the disadvantages of poor thermal stability, small specific surface area (<10 m^2/g) and low porosity limit the application of bulk HPA. Loading HPA onto activated carbon can effectively combine the advantages of the support and the active component and improve the catalytic performance obviously [3]. Carbon also absorbs microwave radiation well.

The physicochemical properties of the resulting catalysts were studied by different methods. The catalytic activity and selectivity of the catalyst were evaluated in the skeletal isomerization of n-hexane in the presence of hydrogen at atmospheric conditions.

This work was supported by the Ministry of Science and Higher Education of Russian Federation (grant no. 075-15-2021-591).

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Hydrogenolysis of glucose to glycols on a magnetically recoverable polymeric catalyst

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Being the most abundant component of lignocellulose biomass, cellulose plays a vital role not only in the utilizing of renewable resources, but also in providing additional opportunities for the production of different molecules-platforms through catalytic processes such as hydrogenolysis, oxidation, or selective reduction [1]. Glycols are the most important raw materials for many branches of modern industry. Ethylene glycol (EG) and propylene glycol (PG) are used in large volumes for the production of medicinal substances, surfactants, antifreeze, lubricants, solvents, fuels, and synthesis of polyester fibers and resins [2]. EG and PG can be obtained under one-pot conditions by hydrogenolysis of cellulose or polyols in the presence of heterogeneous catalysts [1, 3]. In the processes of hydrogenolysis of cellulose to glycols, Ru-containing catalytic systems are considered to be active catalysts [4, 5].

Despite numerous works devoted to the cellulose hydrogenolysis process, only some of them describe reaction kinetics. This is explained by the complexity of the process and the simultaneous behavior of different reactions. In this work, we present the results of the kinetic study of glucose hydrogenolysis into ethylene- and propylene glycols in the presence of Ru@Fe_3O_4/HPS catalyst as a part of the process of catalytic conversion of cellulose into glycols. The structure of the Ru-containing magnetically separable Ru@Fe_3O_4/HPS catalysts supported on the polymeric matrix of hypercrosslinked polystyrene was studied to propose the reaction scheme. As a result of this study, a formal description of the glucose hydrogenolysis process into glycols was performed. Based on the data obtained, the mathematical model of the glucose hydrogenolysis kinetics in the presence of Ru@Fe_3O_4/HPS was developed and the parameter estimation was carried out. The synthesized catalyst was found to be characterized by the enhanced magnetic properties and higher catalytic activity in comparison with previously developed catalytic systems (i.e., on the base of SiO_2). The summarized selectivity towards the glycols formation was found to be ca. 42% at 100% of the cellulose conversion in the presence of Ru@Fe_3O_4/HPS.

The synthesis method of catalyst (Ru@Fe_3O_4/HPS) was developed. Synthesized magnetically recoverable supports and catalysts were characterized by different physical-chemical methods. The use of this catalyst in the process of microcrystalline cellulose hydrogenolysis in subcritical water at 255 °C, 60 bar hydrogen pressure in 50 min allows PG and EG selectivities of 20.0 and 22.6%, respectively, at 100% of cellulose conversion. The catalyst is stable under hydrothermal conditions of the process; it is easily separated from the liquid phase with the external magnetic field and can be reused.

The formal description of the kinetics of glucose hydrogenolysis as one of the stages of cellulose conversion into glycols was obtained. The mathematic model of glucose hydrogenolysis to glycols in the presence of Ru@Fe_3O_4/HPS was proposed. The kinetic parameter estimation was performed according to the model developed.

The results obtained can be used for the development of the effective technology of natural polysaccharides conversion into chemicals and fuels.

This work was supported by RFBR, grant number 20-08-00079.

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Catalytic carbon dioxide conversion to carbon monoxide of hydrolytic lignin in the presence of iron triad compounds

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The most important problem of modern ecology and chemical technology is the rational use of unclaimed carbon materials, such as oil residues, household waste, low-grade coal, etc. One of the large-scale unclaimed carbon materials is hydrolytic lignin, a waste product of the woodworking industry. One of the promising methods of utilization of unclaimed carbon materials is its interaction with CO_2 with the formation of the main product – CO, which is an important preproduct of the chemical industry. The interaction of carbon dioxide with lignin requires harsh conditions for the implementation of a significant conversion (about 1000 °C). The use of catalysts deposited on the surface of carbon materials leads to a noticeable decrease in the process temperature [1].

Previously, it was shown that transition metal compounds exhibit catalytic activity in the gasification reaction of activated carbon [2]. Catalysts based on iron triad metals (Fe, Co, Ni) have a number of advantages: low cost, relatively high activity, non-toxicity with respect to the environment. The purpose of this work is to obtain iron, cobalt, and nickel compounds deposited on hydrolytic lignin and to study the resulting catalytic system in the process of carbon dioxide gasification.

The deposition of metals (Fe, Co, Ni) on hydrolytic lignin was carried out by impregnation according to moisture capacity from solutions of nitrates of the corresponding metals (the mass fraction of metals was 1.3.5.7 wt.%.). Next, the samples were dried for 24 hours at a temperature of 100 °C. Catalytic tests were carried out in a flow-through quartz reactor (inner diameter 10 mm, CO_2 flow rate 30 ml/min) at a temperature of 700 °C and atmospheric pressure. The resulting systems showed high catalytic activity in the process of carbon dioxide conversion. The conversion of CO_2 with the catalyst – Fe compounds (7 wt.% of Fe) increased by 50% relative to lignin without catalyst (800 °C). Cobalt and nickel (7 wt.%) containing samples shown growth of CO_2 conversion also up to 45% relative to pure lignin (800 °C) [3].

The obtained materials before and after the reaction were studied by a number of physicochemical methods of analysis: XRF, DTA-TG (in air and in CO_2), SEM-EDX. X-ray diffraction analysis of the residues after the reaction showed the presence of metals Fe, Co, Ni in the corresponding samples in the forms: Fe_3O_4, CoO, NiO. SEM-EDX showed the uniformity of deposition of metal compounds on the surface of hydrolytic lignin before the reaction.

Thus, gasification is a promising technology for the optimal use of unclaimed carbon materials with the production of products with higher added value, however, it has a number of limitations, one of them is the high temperature of the process, which negatively affects the applicability of the technology. The use of catalysts makes it possible to reduce the process temperature by 150–200 °C. The application of catalytic carbon dioxide gasification to such valuable large-tonnage industrial waste as hydrolytic lignin will deepen and expand the ways of its possible industrial use, and will also allow extending this approach to other unclaimed carbon materials, such as used thermoplastics, asphaltenes, municipal waste, etc.

This work was carried out with a financial support by the Ministry of Science and Higher Education of the Russian Federation (project no. 075-15-2021-591).

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Modification of nickel catalysts for reductive amination based on polymer supports

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In recent years, interest in resource-saving processes for the synthesis of various chemical compounds, and in particular in the reaction of reductive amination, has greatly increased [1–4]. To increase the rate of the synthesis process, activity and selectivity with respect to the target product, some of the catalyst samples have to be modified [5,6].

To introduce additional amino-containing groups into the structure of hypercrosslinked polystyrene, a chlorinated sample of hypercrosslinked polystyrene (20 g) was used, which was placed in a glass tube and heated in an ammonia atmosphere to 200 °C. A glass tube was connected to a flask filled with a sulfuric acid solution to neutralize the ammonia. Modification of hypercrosslinked polystyrene was carried out for two hours, then the reaction tube was cooled to ambient temperature. The HPS sample was washed on a Schott filter and dried in vacuo. Samples of the ammonia-modified hypercrosslinked polystyrene were designated HPS-N.

The HPS samples modified with hydrogen peroxide and chlorine are characterized by weak ammonia chemisorption peaks. The HPS sample modified with ammonia is characterized by a weak chemisorption response of carbon dioxide in the range of 130–180 °C. The original sample of HPS shows an extremely low surface acidity of 0.02 µmol (NH_3)/g(HPS), modification of HPS with hydrogen peroxide leads to a corresponding increase in surface acidity to 0.27 µmol (NH_3)/g(HPS), modification of HPS with chlorine leads to an increase in surface acidity to 0.62 µmol (NH_3)/g(HPS). Ammonia-modified HPS showed an increase in surface basicity from 0.01 µmol (CO_2)/g(HPS) to 1.25 µmol (CO_2)/g(SPS).

The synthesized Ni-based catalysts are characterized by a similar Ni concentration ranging from 20.1 wt.% to 23.2 wt.%. Some increase in the Ni content may be due to the presence of surface-active groups in the case of modified hypercrosslinked polystyrene. The mesopore surface area decreases from 126 m^2/g to 69 m^2/g in the case of surface modified hypercrosslinked polystyrene.

The same phenomenon is observed when changing the surface area of micropores for modified and unmodified hypercrosslinked polystyrene. An increase in the surface area may be associated with an increase in the number of nanoparticles in the case of surface modification with HPS, which can be confirmed by an increase in the amount of available active metal from 0.064 mmol (H_2)/g(cat) to 0.012 mmol (H_2)/g(cat).

A study of the oxidation state of Ni showed partial reduction of nickel acetate in a hydrogen atmosphere for all samples. The original HPS-Ni-25% sample contained nickel acetate in the HPS matrix, while nickel oxides and metallic nickel were present after reduction of the sample with hydrogen.

The catalytic preparation of N-methylglucosamine using Ni-containing catalysts showed a significant increase in the rate of the synthesis process for all samples compared to unmodified Raney-type nickel. The increase in speed can be associated with a corresponding increase in the surface concentration of the active metal. In addition, there was some increase in the selectivity of the catalyst towards N-methylglucosamine. The significant improvement in N-methylglucosamine selectivity can be explained by the increase in the required hydrogenation reaction rate, while the reaction rate of the D-glucose to D-fructose isomerization process remains unchanged.

Thus, modification of the surface of the hypercrosslinked polystyrene leads to a corresponding increase in the surface concentration of nickel. An increase in the surface concentration of the active metal leads to an increase in the rate of the catalytic synthesis of N-methylglucosamine and the selectivity to N-methylglucosamine. The selectivity of the process with respect to N-methylglucosamine is closely related to the rates of the side reaction of D-mannitol formation. In the case of a high surface concentration of the active metal, the direct reaction of the synthesis of N-methylglucosamine predominates, and the side reaction of the formation of D-mannitol is partially suppressed. It was found that the achieved rate for the most active catalyst is 0.27 s^{-1}, and the selectivity of the catalysts to N-methylglucosamine is 98%.

The work was supported financially by AS Fond-M (contract 16436GU/2021 dated May 28, 2021).

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Design of catalysts based on silver nanoparticles and diatomite for photocatalytic decomposition of phenol

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Phenol is one of the most important organic compounds that is widely used in industry. However, it poses a serious threat to many ecosystems, water supply, the environment and human health due to its toxicity, inertia, ability to destroy the endocrine system, teratogenicity and mutagenicity [1]. In this regard, it is relevant to develop an effective method for removing phenol from wastewater. The photocatalytic decomposition of phenol is one of the promising methods of controlling phenol emissions. Recently, there has been a growing interest in silver-containing photocatalysts. Ag-containing photocatalysts are known as water purification catalysts operating under visible light [2]. Silver is often used in conjunction with oxides such as TiO_2, Fe_2O_3, ZnO, etc., which increase the stability of Ag_2O and improve its photocatalytic properties. In this context, the joint use of silver and iron (III) oxide seems quite promising. Fe_2O_3 is widely used due to its magnetic properties, and is also well known for its catalytic and photocatalytic properties. This oxide has a band gap of 2.2–2.7 eV and directly acts as an active photocatalytic material of visible light.

The aim of this work was to design Ag-Fe_2O_3 catalysts for the photocatalytic degradation of phenol. A series of Ag- and Fe_2O_3-containing photocatalysts based on diatomite was synthesized by incipient wetness impregnation with varying the order of introduction of the components (sequential impregnation, co-impregnation and reducing impregnation). The synthesized samples were studied by a number of physico-chemical methods, including the low-temperature adsorption of nitrogen, XRD, TPR, UV-vis spectroscopy, etc. The photocatalytic properties of catalysts were studied in the phenol decomposition under solar-like light.

By the method of low-temperature nitrogen adsorption, it was shown that the synthesized samples are characterized by a hysteresis loop H3 on the isotherms of adsorption-desorption of N_2 which are typical for macroporous samples. When active components were supported, the specific surface area and pore volume decreased (from 25 m^2/g to 13 m^2/g and from 0.062 cm^3/g to 0.057 cm^3/g respectively), which indicates the distribution of active components on the surface of the diatomite, as well as partial blocking of pores by active components.

It was shown by the XRD method that the structure of the diatomite is mainly represented by phases of amorphous silicon oxide (silicate halo 16–30) and quartz phases (peaks at 26.6, 36.5, 39.4, 45.5, 50.2, 54.8 ° 2θ). In addition, iron silicate inclusions were also found in the diatomite structure (peaks at 27.4, 29.9, 37.4 ° 2θ), which may lead to the catalytic activity of pure diatomite. For diatomite modified with iron oxide the peaks of Fe_2O_3 phase were detected on XRD patterns (33.2, 35.5, 54.1, 62.6, 64.2 ° 2θ). At the same time, the Fe_3O_4 and FeO peaks were not detected, which indicates that iron oxide on the surface of the diatomite is formed mainly in the form of the Fe_2O_3 phase. High-intensity narrow peaks at 38.5 and 44.6 ° 2θ were also detected on the X-ray images of silver-containing samples, which indicates a formation of silver particles on the surface of the diatomite.

Thus, the synthesized samples are characterized by the presence of interacting iron (III) oxide and silver particles distributed on the surface of the diatomite. Such interaction affects the redox properties of catalysts and, accordingly, will have a positive effect on their catalytic and photocatalytic properties.

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Investigation of the effect of mass transfer rate on the process of flax shives hydrogenation with a Ni/C catalyst

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Herbaceous plants are an attractive feedstock for producing bioproducts and, as they are fast growing crops. Flax shives is the main waste (up to 70 wt.%) in the production of flax fiber. It composition includes lignin (~25%), cellulose (50%), and hemicelluloses (20%).

Complex processing of all components of the lignocellulose biomass is achieved via its catalytic fractionation based on hydrogenation with hydrogen and hydrogen-donor solvent [1, 2]. This process leads to depolymerization of lignin occurs with the formation of liquid hydrocarbons while retaining the main part of the cellulose.

In this work, we studied the influence of the granule size of the nickel catalyst supported on the oxidized graphite-like carbon Sibunit-4, as well as the stirring rate on the fractionation of flax shives in ethanol with hydrogen at 225 °C.

Nickel catalyst based on oxidized carbon material Sibunit-4 were prepared by incipient wetness impregnation using an aqueous solution of $NiCl_2$ $6H_2O$ followed by sample drying at room temperature for 3 h and at 60 °C for 12 h.

It is shown that a growth in the rotation speed and a decrease in the granule size of the catalyst increase the degree of delignification and, accordingly, reduce the lignin content in the solid residue.

The dependences of cellulose yield on mass transfer conditions are more complex. The best compromise on cellulose yield and degree of delignification (85 and 86% respectively) is achieved with a minimum granule size (54–96 μm) and an average stirring rate (500 min^{-1}).

The yields of liquid products in the catalytic process increase (from 14.62 to 24.63 wt.%) with an increase in the mass transfer rate (from 125 min^{-1} to 1000 min^{-1}. In this case, a change in the granule size (from 1–2 mm to 54–96 μm) of the catalyst does not have a significant effect on the yield of liquid products.

The GC-MS results showed that 4-propenylguaiacol is the predominant product at low stirring rates and large granule sizes of the catalyst with a maximum value at (500 min^{-1} and 100–250 μm). The yields of 4-propylguaiacol increase with increasing stirring rate and catalyst granule size. 4-propanolguaiacol is registered only at high mass transfer rates (1000 min^{-1} and 56–94 μm).

Based on the obtained data of the mass transfer intensity effect on the composition of monomeric products, a scheme for their formation on a bifunctional nickel catalyst is proposed. The lignin structure is cleaved to form active coniferyl alcohol, which is successively converted to 4-propanol guaiacol, 4-propenyl guaiacol and further, to the final product – 4-propyl guaiacol.

Comparison of the influence of the catalyst granule size and the stirring rate on the process shows that both of these factors affect the efficiency of this process and the selectivity of monomeric compounds.

The reported study was supported by Russian Science Foundation, Grant No 20-63-47109.

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ZrO_2- and TiO_2-supported Pd-catalysts for 5-hydroxymethylfurfural oxidation: Effect of support and catalyst treatment

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Due to the depletion of non-renewable resources, the greenhouse effect and global environmental pollution, the “green” chemistry approaches are gaining attention. As an alternative to fossil resources, biofuel can be used, with the process of biofuel production being associated with the formation of useful byproducts. One of those byproducts is 5-hydroxymethylfurfural (HMF) that can be catalytically oxidized to 2,5-furandicarboxylic acid (FDCA) being a promising intermediate to produce bio-based polyesters [1]. To date, a wide variety of catalytic systems for HMF oxidation to FDCA have been discussed, with the supported noble metal-based catalysts possessing noticeable advantages [2, 3].

A large number of factors affect the catalyst performance, including the nature of active component and support as well as catalyst treatment. This work is devoted to designing the supported catalysts for HMF oxidation to FDCA. The effect of support nature and catalyst treatment on the catalytic performance is considered.

The catalysts were synthesized by the incipient wetness impregnation of a support with a solution of palladium chloride in hydrochloric acid. Titanium and zirconium dioxides were used as supports. The Pd amount in all catalysts was 2 wt.%. The samples after impregnation were dried at 150°C and then reduced with CO/He at 300°C (Pd/TiO_2(d), Pd/ZrO_2(d)) or calcined in air at 450°C followed by the reduction with CO/He at 300°C (Pd/TiO_2(c), Pd/ZrO_2(c)). The samples were studied by low-temperature nitrogen adsorption and XRD. The catalytic experiments were carried out in the Parr 5500 HR compact reactor under similar conditions: 80°C, substrate/catalyst molar ratio = 25, $NaHCO_3$/substrate molar ratio = 4, and oxygen pressure of 5 atm. The HMF conversion and yield of FDCA were determined based on HPLC data.

The prepared samples are characterized by a mesoporous structure and a specific surface area of 44–47 m^2/g. According to XRD data, there are no peaks of metallic palladium in the X-ray patterns of the catalysts prepared, which can be explained by high Pd dispersion.

The catalytic experiments indicated that Pd/ZrO_2(d) and Pd/TiO_2(d) samples showed better catalytic performance as compered with the corresponding calcined samples, while TiO_2-supported catalysts showed noticeably lower HMF conversion and selectivity towards FDCA as compared with the ZrO_2-suppored composites. The Pd/ZrO_2(d) sample demonstrated the most efficient catalytic performance: 97% HMF conversion and 68% selectivity towards FDCA in 22 h of reaction. For Pd/ZrO_2(c) sample, the HMF conversion was ~95% and the selectivity towards FDCA was 65%, with the lower catalytic activity and selectivity being caused by the formation of larger Pd clusters during the sample calcination in air prior to its reduction.

In general, the results obtained indicated that the ZrO_2 support contributed to the formation of active and selective palladium sites, with the catalyst treatment additionally affecting the catalyst performance. The possible reasons for the observed phenomena will be discussed in the report.

This work was supported by the Russian Science Foundation, grant No. 19-73-30026.

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Framework-structured phosphates for the dehydration of ethanol into ethylene: relationship between acidic and catalytic properties

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With increased availability and decreased cost, ethanol is potentially a promising platform molecule for the production of a variety of value-added chemicals such as hydrocarbons, 1- butanol, acetaldehyde, acetone, acetic acid and so on [1]. Ethylene is crucial material for the petrochemical industry, which is derived mainly from steam-cracking of petroleum or natural gas feedstocks. Nowadays, with the shortage of natural resource and energy, catalytic dehydration of ethanol, especially bioethanol, to ethylene has become a more competitive and promising route, and therefore has been drawing much attention [2].

Heterogeneous catalysis plays a fundamental role in developing and improving processes to produce renewables from bioethanol. According to the literature, range of catalysts have been investigated in ethanol conversion, such as zeolites, mixed metal oxides, metal catalysts on different supports. In addition, there is a growing focus on complex phosphates with framework structure. The ability to heterovalent substitution is particularly important for their use as catalysts, since this allows to vary the number and strength of acidic and ox-red centers on the surface [3].

In this work, we investigated the physic-chemical properties of complex NASICON-type phosphates with general formula $M_{0.5(1+x)}Al_xTi_{2-x}(PO_4)_3$ (where M – Ni, Mn, Cu; x = 0; 0,2) and their influence on the selectivity for the ethanol conversion products. The catalysts were characterized by X-ray diffraction analysis (XRD), IR spectroscopy, BET method, DRIFT spectroscopy of adsorbed CO, and EPR. The catalytic tests were performed at atmospheric pressure in a tubular flow reactor in temperature range from 280 to 420 °C. The reaction products in the gaseous phase were analyzed by a gas chromatograph Chromatec-Crystal 5000 equipped with flame ionization and thermal conductivity detectors.

The samples were found to belong to orthophosphates with the NZP structure. IR spectra show the absence of amorphous impurities. The materials are mesoporous and have a specific surface area in the range from 6 to 35 m^2/g. For all the phosphate catalysts the converted products mainly consisted of ethylene, as the dehydration product. The addition of aluminum increased total ethanol conversion and promoted the formation of dehydration products. Based on the results obtained, the highest selectivity for ethylene formation (S = 78% at 400°C and $W_\Sigma = 66\%$) was obtained on the $Mn_{0.6}Al_{0.2}Ti_{1.8}(PO_4)_3$ catalyst with highest specific surface area. The mechanism of the catalytic process is proposed. The relationship between the catalytic properties, the composition of phosphates, the acidity and the number of catalytic cites (Lewis and Brønsted) is discussed.

This paper has been supported by the RUDN University Strategic Academic Leadership Program.

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Synthesis of NiS/$Cd_{0.4}Mn_{0.6}S$ and CuS/$Cd_{0.4}Mn_{0.6}S$ photocatalysts for hydrogen evolution from aqueous solution 0.1M Na_2S/0.1M Na_2SO_3 under visible light irradiation

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The rapid depletion of oil resources necessitates extensive mastering of alternative energy and raw material sources for the chemical industry. Serious attention is presently given to use of hydrogen as a fuel. An advantage of hydrogen is its high heating value. Furthermore, the product of its combustion is water, an environmentally friendly substance. The photocatalytic decomposition of water to hydrogen and oxygen using solar energy is promising, but catalytic activity in this process is quite low due to the recombination of photogenerated charge carriers on the semiconductor surface. The addition of sacrificial agents in the system reduces the rate of charge recombination and increases the rate of hydrogen evolution [1].

The solid solution of CdS and MnS, $Cd_xMn_{1-x}S$ allows one to control the composition as well as a band gap which makes it possible to vary the positions of the valence and conduction bands. Recently we synthesized and studied photocatalysts $Cd_xMn_{1-x}S$ (x = 0–1) in the hydrogen evolution reaction under the visible light [2]. The sample with x = 0.6 demonstrated the highest rate of hydrogen evolution. To increase the activity of the solid solution, the surface of $Cd_{0.4}Mn_{0.6}S$ was modified with nickel and copper sulfides by the method of ion exchange between $Ni(NO_3)_2$/$Cu(NO_3)_2$ and Na_2S. The mass fraction of the NiS/CuS varied from 0.1 to 10%. For comparison, a platinum-containing 1%Pt/$Cd_{0.4}Mn_{0.6}S$ sample was synthesized by chemical reduction of H_2PtCl_6 with $NaBH_4$. The concentration of hydrogen was determined by means of Khromos gas chromatograph (Russia) equipped with thermal conductivity detector with argon as the carrier gas.

The activity of photocatalysts was studied in the process of photocatalytic hydrogen evolution from a 0.1M Na_2S/0.1M Na_2SO_3 suspension under visible light with a maximum wavelength of 425 nm. The precipitation of nickel and copper sulfides leads to a significant increase in the rate of photocatalytic hydrogen evolution and is 28.5 μmol min^{-1} for the 0.5% NiS/$Cd_{0.4}Mn_{0.6}S$ photocatalyst, the quantum efficiency was 15.4%. The most active photocatalyst supported by particles of copper sulfide 1% CuS/$Cd_{0.4}Mn_{0.6}S$ showed activity at the level of 7.2 μmol min^{-1} (AQE = 4.3%).

The stability of photocatalysts was studied in cyclic experiments. It was shown that NiS/ $Cd_{0.4}Mn_{0.6}S$ samples are stable in hydrogen evolution from an equimolar Na_2S/Na_2SO_3 mixture, in contrast to the 1% Pt/$Cd_{0.4}Mn_{0.6}S$ sample, for which noticeable deactivation associated with coarsening of platinum particles during flow reactions. Thus, the most effective synthetic approach modification of the $Cd_{1-x}Mn_xS$ surface is the deposition of nickel sulfide particles, which in the future can be considered as a replacement for expensive noble metals.

This work was carried out within the framework of the state task of the Institute of Catalysis, Siberian Branch, Russian Academy of Sciences (project AAAA-A21-121011390009-1).

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Pentene oligomerization over nickel-containing Y zeolite

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Light olefin oligomerization is a good efficient technology for the production of environmentally friendly synthetic fuels such as gasoline, jet fuel and diesel fuel that are free of sulfur and aromatics. Phosphoric acid occurring on silica (also fast as solid phosphoric acid -SPA-) was the first industrial oligomerization catalyst developed by UOP in 1935 [1]. However, this phosphoric acid catalyst has various developments such as short life, corrosion of equipment, difficulty in removing the catalyst from the reactor and its disposal. In the 1980s Mobil structure structure developed a heterogeneous ZSM-5 zeolite catalyst that produces oligomers in the gasoline or diesel fraction by simply adjusting the operating conditions of their MOGD process. Unfortunately, zeolite catalysts are rapidly deactivated, open spaces, inclusions of the zeolite crystal lattice to move oligomer molecules and block zeolite micropores [2]. In recent years, severe cases of the synthesis of micro-mesoporous zeolites have been developed, which make it possible to reduce diffusion complications [3].

The aim of this work is to develop an efficient oligomerization of pentenes under the action of catalytic systems based on zeolites with a hierarchical porous structural structure.

Within the framework of research on the development of heterogeneous catalytic systems for the oligomerization of amylenes, catalysts based on granular Y zeolite with a hierarchical (micro-, meso, macro) porous structure modified with nickel in cationic and oxide forms were prepared.

Obtained catalytic systems characterized by infrared spectroscopy, optical diffraction, optical fluorescence, low-temperature absorption-desorption of nitrogen (77 K). The acid properties of samples of zeolite catalysts are investigated by thermally programmed desorption (TPD) of ammonia and IR spectroscopy for the detection of pyridine.

It has been shown that among the decationized Y samples, the highest activity and selectivity for oligomers in the oligomerization of C_5 olefins is exhibited by the deeply decationized (with the degree of exchange of Na^+ ions for H^+ $\alpha_{Na} = 0.96$) hierarchical catalyst H-Yh: the conversion in pent-1-ene oligomerization was 100%, and the selectivity of the formation of oligomers $n \geq 3$ – 30% at 150°C, 10% wt. catalyst; in the oligomerization of isoamylenes, the conversion is 95%, the selectivity for the formation of oligomers $n \geq 3$ is 17% at 60°C, 20% wt. catalyst.

Among the nickel-containing samples, the most active catalysts were NiNa-Yh with a nickel concentration of 14%, 16% obtained from Na-Yh by ion exchange in a nickel nitrate solution: conversion in pent-1-ene oligomerization was 100%, and the selectivity for the formation of oligomers $n \geq 3$ was 35% at 150°C, 10% wt. catalyst; in the oligomerization of isoamylenes, the conversion is 96%, the selectivity for the formation of oligomers $n \geq 3$ is 22% at 60°C, 20% wt. catalyst. The NiNa-Yh catalysts obtained by impregnation with a nickel nitrate solution and subsequent calcination showed extremely low activity in the oligomerization of C5 olefins.

The work was carried out within the framework of state assignment № FMRS-2022-0080 and with the financial support of the Russian Foundation for Basic Research within the framework of scientific project № 20 -33-90120.

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Nickel and copper phyllosilicates as catalysts for selective hydrogenation of unsaturated compounds

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The replacement of «noble» transition metals (Pd, Pt, Rh) on the 'first-row' transition metals such as Ni, Co, and Fe, which are relatively abundantly distributed on Earth, in the composition of catalysts of selective hydrogenation is a promising task of heterogeneous catalysis [1]. Ni-based catalysts have high hydrogenating activity, but low selectivity and rapid deactivation [2]. Transient metals like Ni, Co, Fe and Cu can be easily incorporated into phyllosilicate structure; thus, phyllosilicate starts to become a popular candidate for catalytic application [3].

The purpose of our work was to investigation the catalytic activity of Ni- and Cu-phyllosilicate in the selective hydrogenation of phenylacetylene to styrene. Series of Ni- and Cu-phyllosilicates was synthesized by the method of deposition precipitation by thermal hydrolysis of urea on commercial silica gel. For comparison, NiO- and CuO-containing catalysts were obtained by insipient wetness impregnation. The prepared catalysts were investigated using temperature-programmed reduction (TPR-H_2), X-ray diffraction analysis (XRD), N_2 adsorption-desorption, transmission electron microscopy (TEM) methods. Reaction of hydrogenation of phenylacetylene to styrene was investigated in liquid phase in autoclave at temperatures 100–140 °C and pressure 1.5 MPa in ethanol.

The results of X-ray phase analysis show that the phyllosilicate phase is formed in the samples prepared by the deposition method, and the oxide phase can be observed in the samples obtained by the impregnation method. The morphology of the samples was investigated by the TEM method. For Ni-containing samples obtained by impregnation, the average diameter of nanoparticles was 10 nm. Ni- and Cu-containing samples obtained by deposition precipitation are characterized by a filamentous structure, which also confirms the formation of a phyllosilicate structure.

The Ni-phyllosilicate-based catalyst showed the best catalytic properties: per 1 hour of the reaction was obtained 89.6% conversion of phenylacetylene with a 90.1% styrene formation selectivity. This Ni catalyst was tested for stability over three cycles. The catalyst remained stable in the recycle with a slight loss of conversion while maintaining high selectivity for the target product.

Thus, we have obtained a highly efficient catalyst based on the Ni nanoparticles, which allows the hydrogenation reaction of phenylacetylene to styrene with high selectivity of the formation of the main product styrene, which is a worthy alternative to catalysts based on noble metals.

This research was funded by Ministry of Science and Higher Education (project no. 075-15-2021-591) and by RFBR, project number19-33-60001.

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Hydrocarbon production in supercritical solvent: a new way for deoxygenation

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At the present stage of development, the conversion of oil crop biomass into the fuel is still a promising direction in the chemical industry [1]. The main component of oil crop biomass is triglycerides, which due to their composition can be used as a source for the production of hydrocarbons. The transformation of vegetable oils and fats is one of the ways to produce environmentally friendly automotive fuels with a low content of sulfur, oxygen and aromatic compounds [2]. The deoxygenation process is one of the priority ways to obtain fuel from triglycerides [3]. The resulting hydrocarbon mixture is similar to petroleum diesel fuel in physicochemical and fuel properties. Moreover, it has all the advantages of classical biodiesel (FAME), for example, high cetane number, carbon neutral, high lubricity, etc.

Being a gas-solid-liquid reaction, deoxygenation is strongly influenced by the low solubility of the reaction components, as well as its high resistance to mass transfer due to the high density. Thus, the process is carried out in harsh conditions using high temperatures (300–500 °C) and hydrogen pressure (up to 6.0 MPa). For these reasons, in recent years, researchers have been interested in reducing working conditions, as well as in the possibility of carrying out the process in a hydrogen-free environment. The use of supercritical fluids can help solve the problem, as it reduces the restriction of mass transfer, as well as increases the solubility of hydrogen and increases its availability to the active sites of the catalyst. Moreover, supercritical fluids can serve as hydrogen atom donors, which eliminate the need to use molecular hydrogen [4]. In the literature, the following supercritical fluids have shown high efficiency of deoxygenation of triglycerides and fatty acids: carbon dioxide [5], water, propane and n-hexane [6].

In this work, various solvent mixtures consisting of n-hexane and propanol-2 were studied in the process of deoxygenation of stearic acid. Co-Ni-containing systems supported on a polymer matrix of hyper-crosslinked polystyrene (HPS) by hydrothermal method were selected as a catalyst. The catalysts Co-Ni-HPS with different metal loading (5 wt.% Co-10 wt.% Ni, 10 wt.% Co-5 wt.% Ni, 10 wt.% Co-10 wt.% Ni, 15 wt.% Co-15 wt.% Ni) were used. The reaction was carried out at a temperature of -270 °C, the partial pressure of nitrogen – 3 MPa.

First, the optimal solvent for the deoxygenation process was chosen. The experiments showed that the hexane provided the higher formation of C_{16}-C_{17} hydrocarbons, when the propanol-2 tended to etherificate the fatty acid with further hydrogenation. Then, four bimetallic catalysts were tested in the stearic acid deoxygenation process in supercritical hexane: 5% Co-10% Ni-HPS, 10% Co-5% Ni-HPS, 10% Co-10% Ni-HPS, 15% Co-15% Ni-HPS. The experimental data on the catalyst influence on the stearic acid conversion and product yield showed that the catalysts allow full substrate conversion to be reached within 1 h of the process. The increase in the nickel content increases the substrate conversion rate, while cobalt content practically does not affect the substrate consumption. The liquid phase analysis showed that n-heptadecane was the major reaction product, however, the formation of lower hydrocarbons (C_{10}-C_{16}) was also observed. The increase in cobalt content leads to an increase in n-heptadecane yield decreasing the formation of lower hydrocarbons. However, the decrease in nickel loading in the catalyst (in the case of 10% Co-5% Ni-HPS) decreases the target product yield. Such a decrease can be explained by the formation of unsaturated C_{17} hydrocarbons, while Ni catalyzes their hydrogenation. Thus, it can be proposed that cobalt promotes the formation of long-chain hydrocarbons, while nickel accelerates its hydrogenation.

This work was supported by the Grant of President of the Russian Federation, grant number MK-5151.2021.1.3.

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Hydrogenation of esters to alcohols in the presence of bimetallic Cu-containing catalysts

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The hydrogenation of fatty acid esters and diesters to corresponding alcohols, belongs to one of the most important types of reactions in fine organic chemistry and petrochemistry. In particular, alcohols such as: isoprenol and ethylene glycol (EG) are used as alternative biofuels because they can be produced from renewable raw materials and are also used as intermediates for the synthesis of pharmaceuticals and solvents. One method of obtaining isoprenol and EG is based on the reduction of the corresponding esters either in the presence of stoichiometric reducing agents such as Na and Li complex hydrides and borohydrides, which are unsafe and their use leads to a large amount of waste [1], or in the presence of toxic catalysts based on chromite Cu and Zn (Adkins catalysts). The processes occur under harsh conditions at temperatures in the range of 200-300 °C and H_2 pressures of 140-300 bar [2]. Heterogeneous catalysts are represented by a number of noble metals such as Pt, Ru, Rh [3]. Hydrogenation of dimethyloxalate (DMO) is one of the key steps in the synthesis of EG from syngas. Despite a large number of proposed heterogeneous hydrogenation catalysts in the scientific literature, the search for new highly efficient systems, in particular, with ultra-low noble metal content, as well as not containing noble metals at all is an extremely relevant topic of modern catalysis.

In our work we synthesized bimetallic 1% Pt-5% Cu and 5% Fe-5% Cu catalysts deposited on an inert carrier – SiO_2 and an active carrier – Al_2O_3. Samples of catalysts were prepared by method of sequential impregnation with the subsequent drying and calcination of samples. The prepared catalysts were investigated using temperature-programmed reduction (TPR-H_2), X-ray diffraction analysis (XRD), diffuse-reflectance infrared spectroscopy with adsorbed CO (DRIFTS-CO) and transmission electron microscopy (TEM) methods. Reaction of hydrogenation of DMO to EG was investigated at temperatures 160–200 °C and pressure 3 MPa. in medium – methanol, H_2:DMO = 50:1. Investigation of catalytic activity of synthesized catalysts in reaction of selective hydrogenation of isoprenyl acetate was carried out in liquid phase in autoclave with possibility of sampling at hydrogen pressure of 2 MPa at temperature 170 °C in medium of solvent - methanol. The reaction time was 6 h.

All synthesized mono- and bimetallic copper-platinum, iron-copper samples were catalytically active in hydrogenation of isoprenyl acetate under relatively mild reaction conditions. However, in the presence of bimetallic Cu-Pt catalysts, complete hydrogenation byproducts were predominantly formed. Modification of copper catalyst with iron additives resulted in increase of hydrogenation ability of copper catalyst and selectivity of isoprenol formation. The catalytic properties of Cu-Fe samples were shown to be affected by the nature of the carrier. When Al_2O_3 was used as a carrier, the selectivity of isoprenol increased significantly. The optimal bimetallic catalyst is the sample of 5Cu-5Fe/Al_2O_3 composition, which provides 100% conversion of isoprenyl acetate with high isoprenol selectivity of 82%.

Thus, we have shown that the catalysts are a good alternative to expensive Pd-based hydrogenation catalysts, which conduct the process of selective hydrogenation of alcohols under relatively mild reaction conditions.

This research was funded by Ministry of Science and Higher Education (project no. 075-15-2021-591), by the support of a grant from the President of the Russian Federation for young scientists - candidates of science MK-3311.2021.1.3.

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Conversion of Ethanol to Acetone on Cerium-Zinc Oxide Catalysts

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Acetone is one of the most important chemicals widely used in the petrochemical industry. One of the interesting methods for acetone production is the reaction of the vapor phase conversion of ethanol. The prospect of this method of obtaining acetone lies in the fact that ethanol is a renewable raw material and is obtained in large quantities from vegetable raw materials. It is known from periodic literature that catalysts based on zinc oxide exhibit a high activity of the reaction of the conversion of ethanol to acetone. In this regard, in this work, we studied the effect of cerium oxide on the activity of zinc oxide in the reaction of the conversion of ethanol to acetone. Binary cerium-zinc oxide catalysts of various compositions were prepared by coprecipitation from aqueous solutions of cerium and zinc nitrates. The obtained mixture was evaporated at 95–100 °C, dried at 100–120 °C, and calcined at 250–350 °C until nitrogen oxides were completely released. The resulting solid mass was calcined at 700C for 10 hours. The activity of the synthesized catalysts was studied on a flow unit with a quartz reactor in the temperature range of 250–700 °C. Thus, we synthesized nine binary cerium-zinc oxide catalysts of various compositions from Ce-Zn=1–9 to Ce-Zn=9–1. The reactor was loaded with 5 ml of the studied catalyst 1.0–2.0 mm in size, and its activity in the ethanol steam reforming reaction was studied. The yields of ethanol conversion products, as well as the amount of unreacted ethanol, were determined on a chromatograph with a flame ionization detector and a 2-m column filled with a specially treated Polysorb-1 sorbent. The amount of carbon dioxide formed was determined on a chromatograph with a 6-meter column filled with a Celite sorbent coated with Vaseline oil.

The conducted studies have shown that the reaction products of the conversion of ethyl alcohol on binary cerium-zinc oxide catalysts are ethylene, acetaldehyde, acetone, carbon dioxide and, at high temperatures, destructive decomposition products. The results of the study of the reaction of the influence of temperature on the conversion of ethyl alcohol on cerium-zinc oxide catalysts showed that the reaction of the conversion of ethanol begins at a temperature of 300 °C. At this temperature, only acetaldehyde is formed. With an increase in the reaction temperature, the yield of acetaldehyde passes through a maximum, and the selectivity of the reaction for acetaldehyde decreases. Raising the reaction temperature also leads to the formation of other reaction products. The formation of ethylene and carbon dioxide begins at a temperature of 400°C, and their yields increase with increasing temperature. The formation of acetone begins at a temperature of 350°C and its yield also passes through a maximum with an increase in the reaction temperature. With an increase in the reaction temperature, the yield of carbon dioxide, a product of the deep oxidation of ethyl alcohol, increases over the entire temperature range studied.

The performed experiments showed that the activity of binary cerium-zinc oxide catalysts, in addition to the reaction temperature, also depends on the atomic ratio of cerium to zinc. Thus, the dependences of ethanol conversion and acetone yield on the atomic ratio of cerium to zinc have the form of a curve with two maxima on the catalysts Ce-Zn=2–8 and Ce-Zn=7–3. The maximum conversion of ethanol is observed on the sample Ce-Zn=2–8 and is 87.7%. The highest yield of acetone is also observed on the Ce-Zn=2–8 sample and is equal to 63.7%. The yield of carbon dioxide slightly increases with an increase in the atomic ratio of cerium to zinc and varies within 8.1% (for the sample Ce/Zn=3/7) and 14.7 (for the sample Ce/Zn=7/3). The yield of ethylene increases with increasing atomic ratio Ce/Zn and varies from 14.5% (on the sample Ce/Zn=2/8) to 37.8% (on the sample Ce/Zn=7/3). Thus, based on the studies carried out, it can be said that cerium-rich catalysts are active in the reaction of dehydration of ethanol to ethylene. The dependences of the yield of acetone and the conversion of ethanol on the atomic ratio of cerium to zinc have the form of a curve with two maxima.

Synthesis of acetylene diols in the $Bu_4NOH/H_2O/DMSO$ catalytic system

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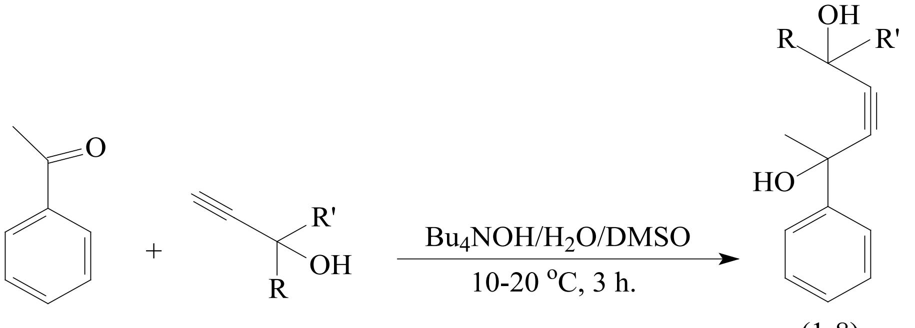
Nowadays, acetylene alcohols are widely used in the preparation of various biologically active organic compounds in the modern organic synthesis [1, 2]. This is due to the fact that they have several active centers in their molecules, including three bonds, hydroxyl group (s) and its active hydrogen which has the capability for an easy reaction to substitution, cyclization, nucleophilic addition and polymerization due to the active hydrogen in the sp-s bond [3].

In this study, the synthesis of corresponding acetylene diols (1-8) based on the reaction of acetophenone with 1-ethynylcyclohexanol (1), 2-phenylbut-3-yn-2-ol (2), 2-(4-chlorophenyl)but-3-yn-2-ol (3), 2-ethynyl adamantanol-2 (4), 3-ethyldec-1-yn-3-ol (5), 3-methyldec-1-yn-3-ol (6), 3-isopropyl-4-methylpent-1-yn-3-ol (7) and 3-ethylhept-1-yn-3-ol (8) were studied. For the nucleophilic addition reaction of acetylene alcohols with acetophenone were carried out in the solvent DMSO, DMFA and THF, in the presence of Bu4NOH catalyst, duration of the reaction, temperature and molar ratios of the starting materials involved in the reaction were studied. The reaction scheme was proposed as follows [4].



(1-8)

Here: RR′= -cHex (1); R= -Me, R′= -Ph (2); R= -Me, R′= -PhpCl (3); RR′= -Ad (4); R=-Et, R′=-Ht (5); R=-Me, R′=-Ht (6); R=-iPr, R′=-iPr (7); R=-Et, R=-Bu (8)

The practical significance of the results of the study is that the biocorrosion of synthesized compounds in oil refineries, oil storage, transportation facilities, steel structures and equipment has resulted in the development of an effective inhibitor of chemical industry enterprises in reducing the amount of layer-forming components in the circulating wastewater and their application to the development of promising drugs based on aromatic acetylene alcohols.

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Low-temperature steam reforming of C_{2+}-hydrocarbons over high dispersed Rh catalysts

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Gas flaring at gas and oil fields, and refineries is an actual problem today. The issue of flaring mainly concerns associated petroleum gas (APG), which is a mixture of saturated hydrocarbons produced at oil fields. At the moment, one of the most promising ways of efficient utilization of APG is to use it directly at the field to generate electricity and heat at small-scale power plants for matching the field's own needs and supplying the nearest settlements [1]. The use of the initial APG as a fuel is problematic, because it has high content of C_{2+}-hydrocarbons, variable composition and low methane index. To solve this problem, it is proposed to use low-temperature steam reforming (LTSR) of C_{2+}-hydrocarbons that make up APG, with the predominant formation methane-hydrogen mixtures [2]. In the present work the properties of highly dispersed Rh catalysts deposited on various supports were studied in the LTSR of model APG mixtures containing C_2H_6-C_4H_{10} in the excess of methane.

A series of Rh catalysts was prepared by sorption-hydrolytic deposition [3]. The main idea of this method is to form a “noble metal salt + alkaline agent” solution, which is metastable under the given conditions (temperature, concentration) with respect to the precipitation of a homogeneous metal hydroxide. This is due to the kinetic inertness of metal complexes to hydrolysis at room temperature. Since the support surface accelerates the heterogeneous nucleation and growth of metal hydroxide particles, the addition of the support to the reagent mixture initiates hydrolysis, which leads to uniform deposition of metals on the support surface. $Ce_{0.75}Zr_{0.25}O_2$, $Ce_{0.4}Zr_{0.5}Y_{0.05}La_{0.05}O_2$, γ-Al_2O_3, TiO_2 (rutile) were used as supports.

The properties of the obtained catalysts were investigated in the LTSR of model APG mixtures at temperatures of 200–400 °C and WHSV = 2500–5000 ml/(g_{cat}·h). The catalysts were stable and provided complete conversion of C_{2+}-hydrocarbons into CH_4, CO_2 and H_2 at T = 320–350 °C. In addition, the conversion of propane and heavier alkanes over Rh catalysts in the low temperature range (200–300 °C) increases the concentration of ethane in the reaction mixture, which is not observed in the presence of nickel catalysts for steam reforming of hydrocarbons. Apparently, ethane is formed by a parallel reaction of propane hydrogenolysis. Ethane has a higher heating value than methane and can compensate the negative effect of the dilution by carbon dioxide and hydrogen on the characteristics of the fuel mixture. This unique property of Rh catalysts makes it possible to obtain gaseous mixtures containing a certain amount of ethane in steam reforming reactions, which in turn is useful for varying the thermal properties (net calorific value, Wobbe index, methane number) of the resulting fuel mixtures. Experimental data show that ethane is formed by hydrogenolysis reaction.

This work was supported by Russian Science Foundation N. 21-73-00122, https://rscf.ru/project/21-73-00122/.

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Selective low-temperature hydrogenation of 5-HMF to BHMF on Pt-contained catalysts

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5-hydroxymethylfurfural (5-HMF) is a well-known biomass-derived platform substrate, possessing high reactivity due to the presence of three functional groups at once – carbonyl group, hydroxyl group and furan ring 1. The product of selective carbonyl bond hydrogenation – 2,5-bis(hydroxymethyl)-furan (BHMF) – is highly attractive due to its broad applications such as intermediate for polymers, drugs and crown ethers 2. Despite high reactivity of 5-HMF, it is challenging to selectively convert the C=O group into the hydroxyl group and avoid over-hydrogenation of other functional groups.

Our work is focused on selective hydrogenation of 5-HMF to BHMF at room temperature in the presence of low-loaded Pt-containing catalysts. Cerium-zirconium mixed oxide (CZ) was used as catalysts support and synthesized by precursors co-precipitation method; catalysts with a Pt content of 1 wt.% and less were prepared by pH-controlled precursor precipitation method.

During the investigation of the solvent influence it was found that the yield of BHMF increases in the series H2O <i-PrOH <THF <EtOH. A study of the activity of catalysts with different platinum content showed that the highest yield of BHMF (96%) was obtained on 1 wt.% Pt/CZ catalyst after 2 hours of the reaction. It is worth to note that experiments were carried out at room temperature and atmospheric pressure. At the same time, decrease of the platinum content to 0.5 wt.% did not significantly affect the yield of the desired product. Catalyst with Pt content of 0.25 wt.% showed relatively low activity at atmospheric pressure (only 8%), however, when the hydrogen pressure was increased to 0.5 MPa at room temperature the yield of BHMF was 42% after 2 hours and the yield of 90% was achieved after 6 hours of the reaction.

Thus, our research has shown that the high yield of BHMF can be obtained at room temperature and atmospheric pressure on 1 wt.% Pt/CZ catalyst and at hydrogen pressure 0,5 MPa on 0.25 wt.% Pt/CZ catalyst using ethanol as a solvent.

The research was financially supported by the Russian Science Foundation (grant no. 20-63-46013) in the part related to catalyst preparation and the Ministry of Science and Higher Education of the Russian Federation (grant no. 075-15-2021-591) in the part related to catalytic studies.

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Photocatalytic decomposition of vancomycin in the presence of NPs ZnO obtained by pulsed laser ablation

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The rapid development of pharmaceutical industry promotes development and subsequent uncontrolled use of antibacterial drugs that poses a threat for aquatic environment and human health due to the resulting formation of antibiotic-resistant pathogenic bacteria [1]. Today, amongst the most promising ways of water purification from organic pollutants and pathogenic microorganisms are improved oxidation processes, which include creation of strong chemical oxidizing agents. For example, exposure of water to ultraviolet radiation while in the presence of semiconductor heterogeneous photocatalyst, such as nanoparticles titanium dioxide or zinc oxide (NPs TiO_2 or ZnO), stimulates the formation of hydroxyl radicals, hydrogen peroxide and other reactive oxygen species (ROS). However, some questions remain. Which ROS induce photocatalytic action of semiconductor oxide NPs during decomposition organic compounds? To what extent ROS formation is a result of light irradiation? In this study, NPs ZnO, obtained by pulsed laser ablation (PLA) in air [2], was used as a photocatalyst for decomposition of vancomycin – antibiotics from the group of glycopeptides. The results of the photocatalytic activity and vancomycin's degradation were then compared with the formation of OH-radicals and hydrogen peroxide which were determined by spectral luminescent methods the presence of terephthalic acid и KI respectively [3].

The study of spectral-luminescent properties showed that water solution of vancomycin has intense absorption in the range from 180 to 230 nm. This range is mainly due to $\pi \rightarrow \pi*$ transitions in peptide bonds. Long wavelength band peaks at 280 nm, due to the presence of aromatic amino acids. Vancomycin weakly luminesces with a maximum in the region of 330 nm. The photocatalytic experiment was carried out at a catalyst concentration ZnO 5 g/L, irradiation was carried out by LED with "soft" radiation UV-A (λ=375 nm, 51 mW). Before training, the dark sorption of vancomycin at the studied concentrations on ZnO NPs was determined, which leads to a decrease in the optical density of the solution by ~10%. Without a catalyst, the decomposition of vancomycin does not occur, since the molecule does not absorb in this spectral range. Significant changes are observed in the absorption spectrum of the antibiotic in the presence of ZnO. At the beginning of irradiation, long-wavelength absorption of photoproducts appears with band maxima at 316 and 355 nm. Their intensity increased within four hours. In this case, the absorption intensity of the vancomycin band with a maximum at 280 nm decreases. Further irradiation leads to the decomposition of both the original molecule and photoproducts. After 20 hours of irradiation, only the edge of the absorption band shorter than 250 nm is observed. The rate constant of vancomycin decomposition calculated from the 280 nm band was 0.16 h^{-1}. To study the mechanisms of photodecomposition in a parallel experiment, ROS (OH-radicals and H_2O_2) formed upon irradiation of ZnO with the same light source were determined. It was shown that OH-radicals are formed in the ZnO dispersion and in the absence of learning, which is the reason for the antibacterial activity of these NPs [2]. Their concentration is proportional to the concentration of NPs. In turn, irradiation of ZnO NPs leads to an increase in the concentration of OH-radicals up to 2 orders of magnitude, which leads to a high activity of these NPs in photooxidative processes.

This work was supported by the Russian Science Foundation (project 19-73-30026).

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Synthesis of acetylene diols alcohols of the different catalytic systems

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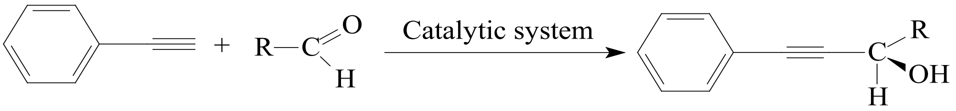
Systematic investigations about the manufacture of various new products on the process of oil, oil products and hydrocarbons or be applying catalysts with higher base in the process for the purpose of subsequent development of classical reactions on the bases of acetylene and its homologs in the near future have been carrying out within the last ten years [1]. Being of great importance acetylene alcohols and such group substances are used on a large scale in different fields, including inhibitors-antibiocorrosion of metal installation in oil-gas industry, ionites purifying poisonous and polluted sewage in the enterprises of metallurgy and oil-gas refinery, as additives increasing low-temperature resistance of aviation gasoline, and in the paint and varnish industry, textile, agriculture, medicine and radio engineering for the various purposes [2].

The aim of the research work is the development of synthesis methods of aromatic acetylene alcohols and their various derivatives using different catalytic systems and also, determining their structure, physico-chemical and biological properties. The most effective way of synthesizing acetylene alcohols is determined using selected complex catalytic systems and also, the range of catalytic activity of used catalysts is created. Acetic aldehyde, croton aldehyde cyclohexonal and benzaldehyde with phenylacetylene reaction of enantioselective etynilation were investiged. Efficiency and course of chemical reaction in the process of formation acetylene alcohol affection of temperature, reaction duration, solvents, catalysts and constituents, their number and nature effects. Based on the results obtained to increase the acetylene alcohol production, reduce the amount of supplementary and intermediate products, the most favorable conditions were found. As objects of study, from the selected acetic and croton aldehydes, cyclohexanal and benzaldehyde with phenylacetylene based on the enantoselective reaction, respectively, new acetylene alcohols− 4-phenylbutin-3, were synthesized (1), 1-phenylhexen-4-yn-1-ol-3 (2), 1-cyclohexyl-3-phenylpropin-2-ol-1 (3) and 1,3-diphenylpropin-2-ol-1 (4). Reaction scheme is proposed below, that is based on literature sources [3].



Where: R= -Me, (1); R= -MeCHCH (2); R=- cHe (3) and R= -Ph (4). Catalytic system – $CsOH/DMSO \cdot H_2O$, $Cs_2CO_3/DMSO \cdot H_2O$, $Et_2Zn/Ti(OiPr)_4/PhMe$, $EtMgBr/Ti(OiPr)_4/PhMe$, $Sn(OTf)_2/NEt_3/MeCN$ and $Zn(OTf)_2/NEt_3/MeCN$.

The selectivity, stability and activity of the used catalysts in the process of alkynylation of selected aldehydes and ketones were studied. The additional reactions taking place that form intermediate and additional products were determined, the effectiveness of the selected catalyst composition was analyzed, and the influence of various factors – temperature, reaction time, and the nature of the solvents – was systematically studied.

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SECTION 3

PHYSICAL-CHEMICAL FUNDAMENTALS OF CATALYSIS

Near ambient pressure XPS and MS study of CO oxidation over model Pd-Au/HOPG catalysts: The effect of metal ratio

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The ability of bimetallic supported catalysts to overperform their monometallic counterparts has induced a great deal of interest to these systems within scientific community. However, despite a large number of investigations of various bimetallic catalysts published in the last decade, the structure of catalytic active sites therein is still under debate. The reason for that is the proneness of bimetallic particles to transformations under the influence of temperature and reaction mixture. PdAu system is among the most studied ones due to its enhanced catalytic properties for a number of reactions, such as vinyl acetate synthesis, low temperature CO oxidation, NO reduction, direct formation of hydrogen peroxide from an H_2+O_2 mixture and others. However, the structure of catalytic active sites even in this prototypic system remains elusive since the actual ratio of the metals on the surface of a working catalyst is not determined unambiguously by the amount of initially introduced metals, but is also strongly affected by the calcination temperature. Moreover, a redistribution of the metals in the particle can occur directly during the course of a catalytic reaction, under the influence of temperature and reaction mixture. To address the problem, operando studies have to be performed. In our recently published papers [1, 2], the model bimetallic Pd-Au/HOPG catalysts have been investigated towards the CO oxidation reaction using a combination of NAP XPS and MS techniques. The samples have shown an onset of catalytic activity at temperatures above 150 °C. CO adsorption on the bimetallic nanoparticles under reaction conditions has been shown to induce segregation that manifested itself as an enrichment of the surface with Pd. It has been shown that heating of the sample under reaction conditions above 150 °C gives rise to the decomposition of the Pd–CO state due to the CO desorption immediately followed by oxidation and simultaneous Pd–Au alloy formation on the surface. Thus, it was clearly demonstrated that it is exactly the alloyed surface that is responsible for the CO oxidation. This conclusion is in line with the Goodman's mechanism which suggests that gold atoms are responsible for the CO adsorption, whereas contiguous Pd sites are responsible for the O_2 dissociation and a further spillover of Oads to Au and/or to isolated Pd sites followed by the oxidation of activated adsorbed CO. However, according to this mechanism, CO oxidation should occur at relatively low temperatures when weak interaction between CO and Au can provide an appropriate concentration of adsorbed CO molecules. But significant surface segregation of Pd atoms induced by CO adsorption can destroy the alloy structure and inhibit the metal surface completely thus effectively deactivating the catalysts. We suggested that such a situation was indeed realized for the samples studied in [1]; the initial Pd/Au ratios at the surface exposed to the reaction mixture were quite large ~1.4 and 3.5 for the studied model bimetallic Pd-Au/HOPG catalysts. In that case, the mechanism of the CO oxidation reaction could switch to that typical of monometallic Pd nanoparticles due to a prominent shortage of Au atoms on the topmost surface layer. In a full agreement with this consideration, both the Pd-Au/HOPG catalysts were inactive towards the CO oxidation in the low-temperature mode, the activity ignited only at temperatures above 150 °C. Finally, it was suggested that the use of bimetallic model Pd-Au/HOPG samples with a lower Pd/Au ratio would lead to increased activity below 150 °C.

In the presented work [3], we have compared the results obtained in the previously published paper with ones obtained for the Pd-Au/HOPG model bimetallic catalyst with a lower Pd/Au ratio on the particles surface. The key goal of this investigation was to find a correlation between the catalytic activity of those model catalysts towards the CO oxidation reaction and the Au/Pd atomic ratio on the surface of bimetallic particles. A systematic elucidation of electronic properties of the elements in bimetallic palladium-gold particles and their depth profiles as well as their transformation induced by the reaction environment of CO oxidation was performed using a combination of NAP XPS and MS techniques for different reaction conditions and initial Pd/Au ratios.

The activities of Pd-Au/HOPG model catalysts towards the CO oxidation reaction are different for the two samples with different initial Pd/Au atomic ratios. More specifically, the PdAu-2 sample with a lower Pd/Au surface ratio (~0.75) is already active starting from 100 °C, while the PdAu1 with a higher Pd/Au surface ratio (~1.0) becomes active only at temperatures above 150 °C. The exposure to reaction mixture at RT induces the palladium surface segregation accompanied by an enrichment of the surface of bimetallic Pd-Au particles with palladium due to the fact that CO adsorption on Pd atoms lowers the nanoparticle total energy. The segregation extent depends on the initial Pd/Au surface ratio. The difference in activity of these two catalysts is determined by the presence and/or higher concentration of specific Pd active sites on the surface of bimetallic particles, i.e., by the ensemble effect. The reverse redistribution of the surface composition observed after cooling down to RT converts the catalysts back to the inactive state, which strongly suggests that the optimum active sites emerge under reaction conditions.

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In situ XPS and DFT study of deNO$_x$ process on platinum catalysts on oxide supports

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Internal combustion engines are the main source of kinetic energy for vehicles nowadays. In the process of their operation, in addition to the main products of fuel combustion, pollutants are also emitted. Special attention is paid to the nitrogen oxides due to the high toxicity of these substances. Thus, the emission of NO$_x$ needs to be reduced. One of the ways to solve this problem is the usage of catalytic converters for after-treatment of the exhaust to meet emission standards. The improvement of existing as well as development of new effective heterogeneous catalysts require a detailed study of the features of the interaction of reaction mixtures both with the active component and with the support material.

Earlier the difference in catalytic behavior of $Pt/Al_2O_3/SiO_2$ and WO$_x$-promoted $Pt/Al_2O_3/SiO_2$ catalysts in reduction of NO by H_2 was shown [1].

In the present work, the platinum catalysts supported on different oxide supports (γ-Al_2O_3, ZrO_2, WO_3/ZrO_2, Siralox (SiO_2/Al_2O_3), WO_3/Siralox) were studied by *in situ* X-ray photoelectron spectroscopy (XPS) using high-pressure cell in gas mixtures of NO, H_2 and O_2. For the explanation of the obtained *in situ* XPS results by DFT calculations were employed.

Analysis of N1s region recorded during *in situ* XPS study shows single N1s peak with binding energy of ~399 eV for systems on ZrO_2 and WO_3/ZrO_2. This nitrogen state was described as oxynitrides [2]. For the Pt/Al_2O_3 sample two states of nitrogen were found: at ~399 eV and at ~403 eV. The last one was assigned to the NO surface species. It should be noted that the state at 399 eV is stable even after gas mixture evacuation, while the state at 403 eV was observed only in the presence of a gas phase. For the samples at Siralox the traces of 403 eV can be conjectured, probably from the alumina, which is not continuously covered with silica.

DFT calculations confirm formation of oxynitrides for all oxides used in experiments. At the same time, the distinctive feature of γ-Al_2O_3 is the presence of two states of nitrogen in oxynitride composition with large and very large charge compared with other oxynitrides. This works both for the bulk phase and for the surface faces.

The combined XPS/DFT study of Pt catalysts shows the difference in surface composition depending on the nature of the oxide supports, which can be responsible for the distinction of catalytic behavior of the systems in NO reduction reactions.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the governmental order for Boreskov Institute of Catalysis SB RAS (project AAAA-A21-121011390011-4).

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The structural diagnostics of Ni/$Ce_{1-x}Zr_xO_2$ heterogeneous catalysts for CO and CO_2 methanation

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The development of catalysts for methanation of carbon oxides attracts a great attention. CO selective methanation is a promising method for deep purification of hydrogen gas designed for low-temperature proton-exchanged membrane fuel cell. CO_2 methanation is considered as a way of CO_2 utilization with production of synthetic natural gas (SNG). Nickel-based catalysts supported on the $Ce_{1-x}Zr_xO_2$ mixed oxides have been considered as promising systems for the methanation processes. High reducibility of the $Ce_{1-x}Zr_xO_2$ oxides renders them useful for redox processes. The oxygen vacancies on the support surface were suggested to facilitate activation of CO_2 molecules and to assist CO dissociation through their ability to accept oxygen. Metal-support interaction can lead to the appearance of oxygen vacancies at Ni/$Ce_{1-x}Zr_xO_2$ interface and affect catalyst activity. The suggestions about metal–support interaction have been made from X-ray photoelectron spectroscopy studies [1, 2]. Moreover, the possible incorporation of Ni^{2+} cations into the CeO_2 lattice has been suggested from data of Raman spectroscopy [2, 3]. However, there is no data on organization of metal/support interfaces in Ni/$Ce_{1-x}Zr_xO_2$ catalysts, which was obtained by the direct methods of structural diagnostics.

The present work [4] deals with the comprehensive study of the structural organization of the Ni/$Ce_{1-x}Zr_xO_2$ catalysts for the methanation of carbon oxides and of the influence of reducing conditions on their structures. The direct methods of structure diagnostics were used: ex situ and in situ X-ray diffraction (XRD) analysis, atomic pair distribution function (PDF) analysis, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and temperature-programmed reduction (TPR) by H_2.

PDF analysis, XRD, and TEM investigation clearly showed strong metal–support interaction, causing the incorporation of a part of the nickel ions into the $Ce_{1-x}Zr_xO_2$ crystal lattice with the formation of a substitutional solid solution. It was shown that mild temperature conditions of the methanation reactions did not result in significant segregation of Ni^0 nanoparticles. A part of the nickel particles remains incorporated in the fluorite lattice in an ionic state. The insertion of lower-valent Ni^{2+} cations into the $Ce_{1-x}Zr_xO_2$ lattice seems to provoke the generation of additional oxygen vacancies in the $Ce_{1-x}Zr_xO_2$ lattice.

The structural evolution of the Ni/ $Ce_{1-x}Zr_xO_2$ catalysts at standard activation in H_2 atmosphere was studied by in situ XRD, and the results were correlated with the data of H_2-TPR and XPS studies. The reversible reduction of the $Ce_{1-x}Zr_xO_2$ oxide in H_2 atmosphere was revealed, which was facilitated by Ni^0 nanoparticles formed on the support surface. Hydrogen spillover promotes the $Ce_{1-x}Zr_xO_2$ surface reduction near the Ni^0/$Ce_{1-x}Zr_xO_2$ interface.

It was shown that the Ni/$Ce_{1-x}Zr_xO_2$ catalyst exhibited high activity in the CO and CO_2 methanation reactions, which was superior to that of industrial catalyst for the methanation of carbon oxides. The elucidated metal-support interaction and synergism of redox properties of the Ni/$Ce_{1-x}Zr_xO_2$ catalysts are relevant for high activity in the CO_2 and CO methanation reactions.

This work was supported by the Russian Science Foundation (project 21-73-20075).

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PdO_x-CeO_2 species highly dispersed on carbon nanotubes as model catalysts for low-temperature CO oxidation

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Catalysts based on palladium and ceria are widely used in various catalytic reactions including the reaction of air purification from carbon monoxide (CO). Accumulation of CO in the enclosed spaces can be lethal or case serious health problems. Thus, efficient catalysts for CO oxidation at room temperature and under ambient humidity are of high demand. Pd/CeO_2 catalysts are known for their activity in low-temperature CO oxidation, however, optimization of the catalysts composition to decrease the noble metal loading and improve their resistance to water vapor still needs to be considered. In order to address these issues fundamental studies using the model catalytic systems should be performed. In this work we analyzed catalysts with highly dispersed PdO_x-CeO_2 species stabilized on the surface of carbon nanotubes (CNTs) or nitrogen-doped CNTs as model systems for low-temperature CO oxidation, including oxidation reaction in the presence of water vapor.

Carbon nanotubes were prepared by decomposition of ethylene over a 62% Fe-8% Ni-30% Al_2O_3 catalyst at 700°C. For synthesis of nitrogen-doped CNTs a 40 vol.% C_2H_4/60vol.% NH_3 mixture was used. Several techniques were employed for the preparation of PdO_x-CeO_2/CNTs composites with variation of the nature of the solvents (water, acetone) and/or the precipitants (NH_3, guanidine). Palladium nitrate $Pd(NO_3)_2 \cdot 2H_2O$ and ammonium cerium nitrate $(NH_4)_2[Ce(NO_3)_6]$ were used as precursors. The palladium loading was varied at 0.5-20.0 wt.% range. The CeO_2 loading was 20 wt.%. The resulted PdO_x-CeO_2/CNTs composites were analyzed by a complex of physicochemical methods: X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Transmission electron microscopy (TEM), Temperature-programmed reduction by H_2 (TPR-H_2) and CO (TPR-CO). The catalytic properties of the samples were studied in the temperature-programmed reaction of CO oxidation (TPR-CO+O_2) and under isothermal conditions at 20°C in CO+O_2 and CO+O_2+H_2O reaction mixtures.

Application of physicochemical methods showed that deposition of the active components from aqueous solution did not provide the stabilization of ceria particles on the CNTs surface. Only small PdO nanoparticles of ~2 nm in size were detected by XRD. Utilization of acetone as a solvent proved to be more efficient technique. Co-impregnation of CNTs with mixed acetone solutions of Pd and ceria precursors provided the formation of PdO_x-CeO_2/CNTs composites comprising the active components in a highly dispersed state even at high loading of palladium. Stabilization of PdO and CeO_2 nanoparticles less than 2-3 nm in size on the CNTs surface was shown by XRD and TEM. Also, formation of ionic Pd^{2+} species dispersed in ceria particles (Pd^{2+}-CeO_2 species) was observed by XPS and TEM. Sequential impregnation of CNTs with ceria precursor followed by palladium precursor also results in the formation of the dispersed PdO and CeO_2 nanoparticles and Pd^{2+}-CeO_2 species. However, at high Pd loading formation of Pd^0 metallic particles was detected as well.

PdO_x-CeO_2/CNTs composites with highly dispersed active components demonstrated high activity at low-temperature CO oxidation with 50% conversion of CO at temperature below 100°C. Testing of the samples activity under isothermal conditions at 20°C showed stability of the catalytic properties of the samples even in the presence of water vapor in the CO+O_2 reaction mixture.

The collected results imply that the PdO_x-CeO_2/CNTs composites can be considered as promising catalysts for CO oxidation at ambient conditions as well as convenient model systems for the analysis of the active sites of catalysts based on Pd and CeO_2.

This work was supported by Russian Science Foundation grant #21-13-00094 from 20.04.2021.

Discrimination between linear and non-linear catalysis mechanisms in Sonogashira reaction under Cu- and ligand-free conditions

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The coupling of aryl halides with alkynes named as Sonogashira reaction is one of the most widespread ways for obtaining of unsaturated organic compounds with different aryl substituents that are of great importance for modern fine organic synthesis. To the moment, several successful examples of the studies dealing with the development of the most attractive copper- and ligand-free (without additives of phosphines, amines, carbenes, etc.) catalytic systems are presented in literature. However, any well-defined strategy for the development of such catalytic systems is absent due to the absence of regular mechanistic studies of the reaction under the stated conditions. We carried out comprehensive kinetic study of copper- and ligand-free Sonogashira reaction to reveal several mechanistic aspects of the catalytic systems operation mechanism.

By the analysis of the differential selectivity patterns of the reaction under competition of two similar aryl halides or two terminal alkynes (that corresponds to so-called “artificial multiroutness”) the data was obtained on the catalytic cycle steps where the activation of the substrates occurred. In particular, the studies were aimed at the distinguishing between two possible mechanistic pathways of the products formation in Sonogashira reaction. One of them can be labelled as “classical” linear reaction mechanism proposing sequential activation of coupled aryl halide and arylacetylene by the same Pd active center. The second possible alternative is non-linear, so-called cooperative mechanism consisting in the activations of aryl halide and arylacetylene by two distinct Pd species in two co-existing catalytic cycles, analogously to those proposed for Cu-containing catalytic systems. Discrimination of these hypotheses becomes possible by the differential selectivity measurements. If activation of each of coupling substrates proceeds independently in two co-existing catalytic cycles, neither concentration no nature of coupling partner can affect the differential selectivity of two similar competing substrates. Otherwise, the sensitivity of the differential selectivity to the nature and/or concentration of common reagent should be observed, and the character of the dependence is determined by possible reversibility of the elementary step where the competition between two substrates occurs.

When two competing aryl iodides were used, the differential selectivity did not change with varying the nature and concentration of arylacetylene indicating the virtual irreversibility of the elementary step where two aryl iodides competed. Irrespectively linear or cooperative mechanistic hypotheses, activation of aryl iodides under Sonogashira reaction proceeding is proposed through their oxidative addition to Pd(0) complexes. Therefore, the data obtained indicated that under copper- and ligand-free conditions of Sonogashira reaction oxidative addition of aryl halides has the virtually irreversible character. Under competition of two arylacetylenes the differential selectivity of competing substrates or formed form them tolanes was sensitive to the nature of common aryl halide. Such result becomes possible only if competing arylacetylenes are activated by compounds containing aryl moiety from aryl halide being in agreement with the realization of oxidative addition of aryl halide to Pd(0) and corresponds to sequential linear activation of the coupling substrates. Based on the data obtained, the mechanistic schemes for catalytic system operation were proposed. Deducing of kinetic equations describing the reaction differential selectivity in the frameworks of the models proposed and simulations of the reaction kinetics using the equations led to the results that were consistent with the experimentally observed dependencies. Therefore, the well-grounded conclusion can be drawn that the activation of aryl halides and arylacetylenes in copper- and ligand-free Sonogashira reaction was realized through linear mechanism, and the elementary steps where the substrates were activated proceeded as the virtually irreversible.

This work was supported by RSF Grant 21-73-00137.

What factors define the UiO-66's catalytic activity in liquid-phase thioethers oxidation?

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Metal-organic frameworks (MOFs) are a class of porous crystalline materials characterized by an extremely high surface area, which suggests their widespread use for storage and separation of gases [1]. The presence of metal centers in the structure also makes MOFs promising materials for catalytic transformations, including selective oxidation reactions [1].

For UiO family MOFs (UiO-66, UiO-67, etc.), it was shown that their stability, surface area, porosity, adsorption and catalytic properties are related to the number of defects in the structure [2]. In addition, acidic and basic sites can form at defect sites in the MOF structure, which affect the catalytic properties [3].

In this work, we have shown that diffusion limitations are observed in the oxidation of methylphenyl sulfide 30% H_2O_2 in the presence of Zr-MOF UiO-66, and we also estimated the particle size at which their contribution is minimal. We proposed a new method for determining the number of basic sites in UiO-66 based on the liquid phase adsorption of isobutyric acid from hexane. In combination with NMR spectroscopy, this method made it possible to show the nature of the basic sites in UiO-66. We have demonstrated the influence of the total number of defects, as well as the number of basic sites in the presented samples, on the UiO-66 catalytic activity. We have also shown that basic centers do not affect the high selectivity of the reaction towards methylphenyl sulfone.

The methods used in the course of the work made it possible to separate the contributions of the main factors (mass transfer, number of defects, acid-base centers) that define UiO-66 catalytic activity, to study the nature of the catalytic centers of UiO-66 more thoroughly, and to construct a general model describing the catalytic activity of UiO-66 from its structural parameters.

This work was supported by RSCF Grant № 21-73-00239.

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Selective dimerization of ethene to 2-butene on Zn-modified zeolite: a mechanistic study

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A series of large-scale industrial processes including steam cracking of hydrocarbon feedstock yield over 200 million tons of ethene each year [1]. One of the options for ethene effective utilization is its selective dimerization to 1- and 2-butenes which in turn are used as a comonomer in polyethylene manufacturing and in propene production via metathesis reaction with ethene, respectively [2]. Several catalysts have been proposed for the selective formation of 1-butene from ethene, with Ni-exchanged zeolites being one of the most studied systems [3]. However, 2-butenes are also demanded materials for the polymers industry. It is relevant, then, to search for alternative catalytic systems and study other metal-containing zeolites in order to test their ability to convert ethylene to 2-butene.

In this work, selective ethene dimerization to 2-butene was observed on Zn^{2+}/ZSM-5 zeolite with ^{13}C MAS NMR. The joint application of MAS NMR and FTIR methods resulted in the identification of the main species formed prior to 2-butene, which are ethene π-complex with zinc sites and but-3-en-1-ylzinc. Two possible pathways of but-3-en-1-ylzinc formation were considered that were consistent with the spectroscopic data and the literature on Zn-containing zeolites. One mechanism implied zinc-vinyl intermediate formation, while the other one involved bridged dimeric species.

Both alternative routes were studied with the DFT method. The theoretical investigation showed that although both pathways were possible, the most probable reaction route characterized by lower activation barriers for all steps was the following: (i) ethene adsorption on a Zn^{2+} site with the π-complex formation; (ii) the adsorption of the second ethene molecule; (iii) the formation of a saturated bridged C_4-intermediate bound to Zn and O atoms; (iv) the latter species dehydrogenation to give but-3-en-1-ylzinc. The but-3-en-1-ylzinc desorbed as 1-butene which isomerized rapidly to trans- and cis-2-butenes as detected experimentally with MAS NMR and FTIR.

Hence, based on the obtained results, Zn^{2+}/ZSM-5 zeolite represents a promising catalyst for the selective conversion of ethene to 2-butene [4]. The findings of this work will be useful for further applied studies aimed at developing the optimal reaction conditions for the industrial process.

This work was supported by RSF Grant №21-73-10013 and the Ministry of Science and Higher Education of the Russian Federation within the governmental order for Boreskov Institute of Catalysis (project AAAA-A21-121011390053-4).

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Study on the peculiarities of H_2O_2 activation in the presence of zirconium-substituted Keggin heteropolytungstate

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Zr-based catalysts are known for being active and stable in H_2O_2-based selective oxidation, however, the mechanisms of their catalytic actions are still unclear. Owing to their structural analogy with metal oxide surfaces and the possibility of studying them at the atomic level, polyoxometalates (POMs) have served as convenient molecular models for heterogeneous metal oxide catalysts [1].

In this work, we report the study of Zr-substituted tungstate of the Keggin structure $(Bu_4N)_8[PW_{11}O_{39}Zr(OH)(H_2O)]_2$ (Zr_2-POM) and it's potential as a catalyst for H_2O_2-based selective oxidations.

Zr_2-POM was synthesized following the procedure described in [2], the structure was confirmed by FTIR, ^{31}P NMR, and potentiometric titration. Zr_2-POM exhibited high activity and selectivity in the oxidation of a range of alkenes, organic sulfides, and alcohols. The selectivity to the corresponding epoxides in the oxidation of cyclic alkenes (cyclooctene, 3-carene, and *trans*-caryophyllene) with 1 equiv. of H_2O_2 reached 75–95%, while cyclohexanol transformed to cyclohexanone with 100% selectivity, and *cis*-methyl oleate gave the corresponding *cis*-epoxide with 93% selectivity indicating a concerted mechanism of oxygen atom transfer. The predominant formation of epoxide, diol, and 2-ketol in the oxidation of the test substrate, cyclohexene, indicates the predominance of the heterolytic mechanism of H_2O_2 activation in the presence of Zr_2-POM [3].

The kinetic regularities of the oxidation of alkenes with hydrogen peroxide and the unproductive decomposition of H_2O_2 in the presence of Zr_2-POM have been studied. The rate of H_2O_2 decomposition increases with water addition to the reaction system, has fractional (<1) order in the catalyst indicating hydrolysis of the dimeric POM into the monomeric species is the limiting step. Addition of $HClO_4$ to the reaction mixture increased the rate of H_2O_2 decomposition in the presence of Zr_2-POM, while the addition of TBAOH, on the contrary, slowed the process down. Additives influenced the oxidation reaction of cyclohexene in the opposite way: the maximum achievable cyclohexene conversion along with H_2O_2 utilization efficiency increased upon TBAOH addition from 34 and 47% to 46 and 59%, respectively, and these indicators, on the contrary, decreased to 21% and 38% when acid was added.

The interaction of Zr_2-POM with H_2O, H_2O_2, and organic substrates in MeCN was monitored by ATR-FTIR *in situ*. It was found that addition of $HClO_4$ to the reaction mixture accelerates the hydrolysis of dimeric Zr_2-POM with the formation of monomeric species, while TBAOH addition, on the contrary, slows down the process. Thus, the effect of acid and OH^- on the rate of unproductive decomposition of H_2O_2 can be due to the effect of additives on the rate of hydrolysis. The addition of H_2O_2 (1–10 equiv. per POM) to Zr_2-POM resulted in the disappearance of the 768 cm^{-1} feature attributed to Zr−O(H)−Zr and the appearance of a new band at 807 cm^{-1} that can be assigned to ν(O-O) in Zr-peroxocomplex formed. Importantly, this band disappeared after the addition of methyl phenyl sulfide with complete restoration of the band at 768 cm^{-1}, indicating a return to the initial dimer. GC analysis of the reaction mixture showed 99% conversion of sulfide along with 89% yield of corresponding sulfoxide and 10% yield of sulfone, thus indicating that active Zr-peroxocomplex was obtained.

This work was supported by the Russian Science Foundation (grant No. 22-23-00410, https://rscf.ru/en/project/22-23-00410/).

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In situ XRD investigation of nickel-based catalysts activation process

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At present, the search for various energy sources based on renewable natural resources is being actively pursued in order to replace dwindling fossil reserves. One of these sources can be fuel synthesized via the processing of biomass obtained by fast pyrolysis. Ni-containing catalysts are promising candidates for processing such biomass. To improve the textural characteristics of NiO-based catalysts and to change the activity and selectivity in the deoxygenation reaction various additives are often used, which also influence the phase composition of the catalysts. Changes in these parameters, therefore, can also affect the activation process of Ni-based catalysts, which usually takes place in a hydrogen flow.

In the course of this work, the *in situ* studies of structural features of NiO-based nanostructured catalysts and of these catalysts reduction process were carried out. The peculiarity of the systems under study was the stabilization of the oxide in highly dispersed form due to the introduction of silicon additives. X-ray diffraction of the catalyst differed from the "classical" X-ray diffraction of bulk nickel oxide and was characterized by certain features - different broadening of diffraction reflexes - whose interpretation by standard methods did not give satisfactory results. Therefore, the catalyst was investigated by the Debye method X-ray diffraction simulations. The following structural models were considered: (1) particle shape effect using cube, sphere, plate, and filament as examples, (2) different models of silicon embedding into nickel oxide structure. It is shown that silicon incorporation is realized due to NiO layer replacement with formation of a fragment following the "spinel" Ni_2SiO_4 structure fragment. The results of transmission electron microscopy also confirmed this hypothesis and showed that the silicon is evenly distributed on the nickel oxide particles. In addition, the crystallites have a plate-like shape with a thickness of 1.5 nm and a width of 3 nm.

The second task was to carry out in situ X-ray diffraction studies of the reduction process of nickel oxide with the introduction of various additives (W, Si, Cu, Mo). It was shown that SiO_2 addition stabilizes particle size and prevents sintering during the calcination process, while other modifiers affect the reduction process. Thus, the Cu introduction lowers the initial temperature of the nickel oxide reduction process and the introduction of W and Mo leads to the increase of the temperature. The Cu and Mo additions as well influences the phase composition from the very initial state of the catalysts, and, so, influences the phase transitions occurring in the reduction process. Also, it was shown that the solid solutions based on the metallic Ni structure form during the reduction process.

This work was supported by Program "Priority 2030" NSU.

Deep machine learning for microscopy image analysis: services for practical applications in catalysis

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Identifying, counting and measuring particles on microscopy images is an important component of catalytic studies. Processing microscopy data on hundreds of particles from several points of the catalyst is required, the more the better, so common manual analysis can take hours. Therefore, having an accessible and simple tool for automatic object recognition and size measurement can significantly decrease the work of researchers and the time for experiments. Deep machine learning (artificial intelligence) looks very promising for the purpose of data processing automatization.

In the present work deep machine learning approach was developed for the particle recognition on scanning probe microscopy (scanning tunneling microscopy (STM) and atomic force microscopy (AFM)) and transmission electron microscopy (TEM) images [1–4]. Based on the results of the work two unique services for image analysis are developed: web service ParticlesNN (http://particlesnn.nsu.ru) and cloud service DLgram. DLgram allows training the neural network Cascade Mask-RCNN by the users using just a few labeled objects and applicable for any images, not just STM, AFM or TEM [4]. After training, the neural network is able to recognize the rest of objects on the same image, which was used for training, or similar images. Service DLgram uses Telegram messenger as interface (t.me/nanoparticles_nsk). Both ParticlesNN and DLgram are accompanied with detailed instructions for user convenience.

The advantages of the proposed services as compared to other software products are: 1) The noisy images or images with artifacts that are typical for microscopy data without additional processing can be processed; 2) The user does not need coding skills; 3) The services are available to any user, anywhere in the world; 4) The user can adjust automatically determined contours with the help of external software products; 6) Processing results are displayed in the form of tables where information on every identified object is available for users. Obtained tables allow various post-processing depending on the goals of the work (statistical analysis, extraction of the overlapping / separated particles, etc.). Services allow the optional consideration of particles at the image boundary for more correct statistical analysis.

The advantages of using deep learning methods for automatic particle recognition: 1) Analysis is faster (compared to manual analysis); 2) Objectivity of measurements (independent of user personality and experience); 3) The neural network takes into account specific features such as a non-uniform background due to particle projection overlapping or support thickening, etc. This approach to particle recognition using neural networks allows us to improve the quality of recognition over time by accumulating marked data.

Both web service ParticlesNN and service DLgram make the application of this proposed approach ‘user friendly’ and make it possible for any user, anywhere in the world to use the results of our work on particle recognition on microscopy images of the supported catalysts.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation (project AAAA-A21-121011390011-4).

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NAP-XPS and MS studies of model Pd-Ag/HOPG catalysts in CO oxidation

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Nowadays, supported bimetallic catalysts are in the focus of many researches due to their ability to enhance catalytic properties towards numerous industrially relevant reactions. PdAg are promising to improve on catalytic performance compared to their monometallic counterparts in the selective alkyne hydrogenation [1], CO oxidation [2], methanol oxidation [3], selective formic acid decomposition into CO_2 and H_2 [4], and many others. In spite of thorough attempts to rationalize synergistic effects occurring upon introducing a second metal into a monometallic catalyst, their fundamental reasons and regularities still remain a subject of debate. Nevertheless, it is well established that the addition of a second metal results in the emergence of bimetallic active sites with a specific geometry on the nanoparticles surface and a change in their electronic properties. For this reason, most researchers believe that it is detailed studies of the surface of bimetallic nanoparticles that play a crucial role in understanding and rational application of these synergistic effects. The combination of model systems, where nanoparticles of active metals are deposited onto an atomically smooth planar support, together with *in situ/operando* techniques may increase reliability and information content concerning the chemical and surface composition of the active component therein. Among planar supports, which can be successfully used in such investigations, highly oriented pyrolytic graphite (HOPG) occupies a special position [3, 5].

In this work, bimetallic Pd-Ag nanoparticles deposited onto HOPG have been investigated by a combination of mass-spectrometry (MS) and near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) in the stoichiometric reaction mixture of CO oxidation at a total pressure of 0.25 mbar in a temperature range of 25–300 °C to establish the correlation between their catalytic performance and dynamics of the surface composition therein. It was found that the Pd segregation on the surface takes place under reaction condition at room temperature. It escalates at increasing temperature to 150 °C. The relative intensity of the Pd-CO adsorption state observed in the Pd3d core-level XP spectra gradually decreases from maximum at room temperature to zero at 200 °C. The Pd/Ag surface atomic ratio after reaching the maximum value at 150 °C starts to decrease upon a further increase in temperature due to CO desorption and reverse redistribution of the two metals along the depth of the nanoparticles. Mass-spectrometry data shows that the catalyst demonstrates no catalytic activity below 150 °C. The CO_2 signal appears at temperature 200 °C and hits the maximum at 300 °C, when the Pd-CO adsorption component is no longer observed in XP spectra. Thus, the inhibition of low-temperature activity is explained by CO over adsorption that effectively blocks active sites. It is the specific PdAg alloy state formed under reaction conditions that is solely responsible for the CO oxidation activity. Using the STM technique it was clearly demonstrated the HOPG-supported Pd-Ag nanoparticles were stable against sintering under conditions tested up to 300 °C, which makes them useful for further studies in a number of reactions below this temperature.

The authors would like to thank the Russian Science Foundation (Grant No. 19-13-00285-P) for the financial support of this work.

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MTM reaction over multinuclear sites in Cu-exchanged zeolites: DFT survey and spectroscopic analysis

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The Cu-functionalized zeolites is known to be an efficient catalyst for some important redox chemical processes. Among them the direct conversion of methane to methanol (so called MTM reaction) is one of the most attractive applications of such catalytic systems. The high energy required for cleavage of the C-H bond in CH_4 molecule combined with the facile overoxidation to CO_x impose great challenges for the implementation of such process [1]. The ability of Cu-exchanged zeolites to selectively convert methane to methanol was reported for the first time by Groothaert and co-workers [2]. Since that time many researchers' effort have been dedicated to increase methanol yield and selectively using catalyst based on different zeolite frameworks [3–5].

In addition to increasing of the catalyst productivity the nuclearity and structure of active Cu sites is hotly debated in the literature [1, 4, 6]. In the recent work by Pappas and co-workers [1] it was shown that redox active $ZCu^{II}OH$ play the role of precursor for further formation of monomeric and dimeric Cu-oxo species which likely responsible for methane activation. From the other side in few earlier works [6, 7] the trinuclear Cu-sites were proposed to be the most plausible sites for MTM conversion.

In the present work we have considered two reaction paths proposed by Pappas and co-workers [1] which led to the formation of different monomeric and dimeric Cu-oxo species. In addition, we have considered the variety of multinuclear Cu-oxo sites incorporated in proximity of 6MR and 8MR of CHA framework including trinuclear and tetranuclear sites. For all the configurations considered we have computed the Gibbs energy for methane molecule activation and simulate time averaged theoretical XANES signal based on the set of structures extracted from MD trajectories. The estimation of Gibbs energies demonstrated few most energetically favorable candidates among which binuclear and trinuclear Cu-oxo clusters. The simulation assisted analysis of experimental XANES spectra collected for O_2-activated Cu-CHA, demonstrated that experimental signal contributed by the mixture of three-fold and four-fold coordinated Cu-sites. At the same time, it has been demonstrated that clusters nuclearity affect the theoretical XANES signal in the lower extent thus assuming that it is difficult to retrieve the information regarding Cu-oxo complexes nuclearity from experimental XANES data.

This work was supported by RSF (project № 21-73-00309).

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Hydrocarbons adsorption on palladium nanocatalysts: theoretical and experimental IR investigation

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Nanoparticles have a number of advantages over their bulk counterparts, such as surface area and activity. Palladium catalysts are being extensively used for hydrogenation of unsaturated hydrocarbons (e.g., selective hydrogenation of acetylene traces in ethylene-rich mixtures) [1]; a large number of studies was aimed to get structural insights into the catalytic processes [2-3]. An important step in such reactions is the adsorption of hydrocarbon molecules on the palladium surface, since different adsorption geometries can lead to different reaction products. In this work, we report the combined experimental and theoretical study of the industrial catalysts consisting of 2.6 nm supported palladium nanoparticles (NPs) probed by in situ EXAFS, XANES, X-ray diffraction (XRD) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), complemented by DFT calculations.

In situ Pd K-edge XAFS and XRD measurements were performed simultaneously for the Pd/C sample at BM31 beamline of ESRF (Grenoble, France). The sample was loaded inside 2 mm quartz glass capillaries and connected to a remotely controlled gas line. Prior to exposure to hydrocarbons, the samples were activated in 20 mL/min flow of 20% H_2/He at 125 °C for 30 min and then purged by He flow. Then, the sample was cooled down to 50 °C and exposed to pure ethylene flow (20 mL/min).

In situ DRIFTS measurements for Pd/Al_2O_3 were performed on Bruker Vertex 70 spectrometer. Measurements were performed in range 5000–400 cm^{-1} with a 1 cm^{-1} resolution, 40 scans, and automatically transformed into absorption units using the Kubelka–Munk function. The powdered sample (12.8 mg) was loaded into a cell enabling to control the temperature and the gas flow. An external gas system equipped with mass flow controllers was used to set the gas flows of Ar, H_2, and C_2H_4 through the cell. The gas mixture flowed either through the cell with the sample, or through a by-pass. Switching was carried out using 3-way valves.

Atomic structures of the adsorbed C_nH_m molecules on palladium (111) and (100) surfaces and their vibrational spectra were obtained using VASP [4]. 5 layer Pd surfaces in (111) and (100) geometries were constructed with initial Pd–Pd distances a = 2.75 Å and then optimized within conjugated gradient algorithm. The cut-off energy for the plane-wave basis set of 500 eV was used. The Monkhorst–Pack method was used to generate k-points 5×5×1 and 9×9×1 grids for (111) and (100) surfaces, respectively. The convergence criteria were set to 10^{-6} eV for self-consistent field calculations and 10^{-5} eV for geometry relaxation. The infrared spectra of the optimized structures with adsorbed hydrocarbon molecules were simulated keeping all palladium atoms fixed, which was checked not to affect the spectra for several selected cases.

In this work, it was shown that adsorbed ethylene dehydrogenates to C_2H_3, C_2H_2 and C_2H and, finally, decomposes into palladium carbide. The combination of in situ XAFS, XRD and DRIFTS data provided not only complementary information, but also facilitated the mutual interpretation of the data from different techniques. This study reveals the evolution pathway of ethylene on industrial Pd-catalyst under atmospheric pressure at moderate temperatures, and provides a conceptual framework for the experimental and theoretical investigation of palladium-based systems.

This work was supported by the President's Grant of Russian Federation for young scientists MK-5853.2021.1.2 (№ 075-15-2021-499).

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Investigation of Pt/CeO_2-MnO_x catalysts in CO oxidation reaction

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For today, catalytic systems using CeO_2 as support are of great interest to commercial applications and fundamental researches. One of the most important applications of CeO_2-based catalysts is the low-temperature CO and hydrocarbons oxidation reaction using a combination with noble metals. CO and C_xH_y low-temperature oxidation have wide applications in exhaust gas cleaning, energy production, gas sensors, etc. In all cases, the realization of catalytic performance at room temperatures or even below 0 °C is highly demanded.

High activity of the ceria-noble metals composition in oxidations reactions is due to the unique properties of cerium oxide – strong metal-support interaction (SMSI) with active components and high oxygen storage capacity (OSC). These properties allow accumulating absorbed oxygen, which is very important in constantly changing reaction conditions, especially in the low-temperature range. The most effective low-temperature oxidation on PGM/CeO_2 (PGM=Pt, Pd) catalysts occurs in the presence of specific $PGM-O_x$ cluster active centers on the surface and platinum metal ions in the near-surface layers of the support. The formation of such centers, as a rule, occurs when high concentrations of platinum metals are used. Reducing the amount of platinum used while maintaining low temperature activity is an important task. Currently, the modification of CeO_2 is actively applied to improve oxygen capacity and mobility due to the formation of solid solutions with dopants. Manganese is one of the promising modifiers for ceria on the base of similar redox properties of Mn and Ce using the ability of both metals in the reversible transition of oxidation states between 3+ and 4+.

In this work, a series of $Ce_{1-x}Mn_xO_{2-\delta}$ supports were synthesized and studied. Samples were obtained by coprecipitation in an alkaline medium, with a manganese content of 10, 20 and 30% atomic. The samples calcination temperature was varied in the range of 450–600 °C. According to XRD, all samples are single-phase systems and have a fluorite lattice. As the amount of manganese content increases, the lattice parameter of the fluorite phase decreases and the number of microstrains increases. According to the XPS data, the manganese on the surface of the supports is presented in two oxidation states: Mn^{2+} and Mn^{3+}. Also, part of Ce^{3+} decreases when Mn is introduced into the CeO_2 structure. This set of supports were impregnated with 5% wt. platinum as the active component to produce 5% $Pt/Ce_{1-x}Mn_xO_{2-\delta}$ catalysts. According to XRD, no additional platinum-containing phases were observed. Crystalline platinum particles were also not observed using the HRTEM method. According to the XPS data, the platinum on the surface of the catalysts is stabilized in ionic forms only with two oxidation states: Pt^{2+} and Pt^{4+}.

Catalytic testing has shown that the CO conversion curves shift to a lower temperature range when the amount of manganese dopant increases. It was shown, that CO oxidation reaction starts at temperatures below 100 °C. The low-temperature activity was correlated with the amount of mobile oxygen, available in the temperature range 0–230 °C, which is not typical for pure ceria. In the result of catalytic testing was found that the deposition of platinum on the composite supports led to the high activity of catalysts already at room temperature in the CO oxidation reaction. It was proposed that active sites for CO oxidation can be required the different structures and surface states of Pt and Mn/Ce as well.

This work was partially supported by the RFBR and the Government of the Novosibirsk Region joint grant № 20-43-540009 and Ministry of Science and Higher Education of the Russian Federation within the framework of BIC project AAAA-A21-121011390053-4. The study by the HRTEM method was performed using the equipment of the Collective Use Center "VTAN" NSU.

Prediction of the binding energies of CO adsorbed on Pd nanocatalysts using machine learning enforced by an adaptive sampling approach

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Dispersion and surface morphology is one of the key factors influencing the catalytic activity of transition-metal nanocatalysts. One of the laboratory techniques that allow us to study them is a Fourier-transformed infrared (FTIR) spectroscopy of adsorbed probing molecules (such as CO, N_2, H_2, etc) [1]. This technique is based on the fact that adsorbed molecules are perturbated when they are interacting with the metal surface which causes a shift in their frequency compared to that in the gas phase. Shift value depends on what facet or defect site (corners, edges, terraces) adsorption occurs since binding energy there can be different. It allows obtaining information about surface morphology and even size [2, 3].

However, resulting experimental FTIR spectra are also significantly affected by the interaction of adsorbed molecules with each other. Coverage effects depending on pressure and temperature make interpretation and quantitative analysis of spectra complicated. At that time, existing methods of molecular dynamics or density functional theory (DFT) approaches do not allow both fast, computationally cheap, and precise simulations of coverage effects and computations of frequencies and binding energies of perturbated molecules even on real nanoclusters. Thus, estimation of the coverage as a function of P and T is desired for reliable interpretation of spectra.

As the first step for this, we developed an approach that allows predicting the binding energy of adsorbed molecules using machine learning (ML) algorithms [4]. We studied the interaction of CO molecules (one of the most popular probes in this technique) with the Pd_{55} nanocluster (~1.3 nm in diameter. Such nanoparticle contains both (111) and (100) facets, where CO adsorption was studied along with interaction with edges and vertexes. Due to a high dependency of binding energy from the nature of adsorbing site (top, bridge, or hollow) and its local coordination (e.g. bridge on particle edges, or regular Pd(100) and Pd(111) facets), we suggested using a radial distribution functions (RDF) as a descriptor for ML algorithm to describe interposition of CO and Pd_{55}. We also tested several conventional structural descriptors, including mean Pd–C distances, coordination numbers (CN) and generalized coordination numbers (GCN), angular distribution functions (ADF), and their different combinations.

To avoid overtraining and to probe the most relevant positions above the metal surface, we utilized the adaptive sampling methodology for guiding the ab initio DFT calculations. 9 ML algorithms were tested in the task of binding energy prediction, and among them, the support vector machines (SVM) and Extra Trees algorithms provided the best approximation quality and mean absolute error in energy prediction up to 0.12 eV. RDF were better descriptors than others.

Based on the developed potential, we constructed an energy-surface 3D map not only for the whole Pd_{55} nanocluster but also extended it to new geometries, Pd_{79} (~1.8 nm), and Pd_{85} (~2.2 nm), not implemented in the training set. This methodology can be easily extended to adsorption energies onto mono- and bimetallic nanoparticles at an affordable computational cost and accuracy, and it also has a great potential to be further developed for prediction frequencies and FTIR amplitudes.

The research was financially supported by the Ministry of Science and Higher Education of the Russian Federation (State assignment in the field of scientific activity, № 0852-2020-0019).

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The formation and functioning of multicomponent catalytic hydrogenation systems: the ^{27}Al NMR study

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The inferences on the nature of catalytically active species formed in multicomponent catalytic systems are mainly drawn from the model experiments and quantum-chemical calculations [1]. Therefore, in terms of reliability, such information is inferior to that obtained from real catalytic experiments. In addition, many systems are analyzed using *ex situ* methods, which are characterized by violation of reaction conditions during sampling and analysis. Theoretically, such manipulations can lead to major errors in understanding the nature of the complexes, active in a real catalytic system, as well as to contradictory conclusions derived from various methods. Besides, the multicomponent character of such systems significantly complicates interpretation of the results obtained, for example, by such methods as ^{1}H or ^{13}C NMR, since the spectrum of reaction solutions contains a large number of signals, which often merge together because of additional broadening caused by the presence of transition metal atoms and/or exchange interactions [2].

For instance, the ^{1}H or ^{13}C NMR spectra of our catalytic systems, formed on the basis of $M(acac)_2$–Red (M= Co, Cu, Ni or Pd; Red=$LiAlH_4$ and $AlEt_3$), contain signals from solvents (usually these are mixtures of toluene or benzene with hexane or THF), acetylacetonate or ethyl ligands and substrate. Given that the nanosized particles of transition metals are formed in the above systems (TEM and EPR data), their ^{1}H or ^{13}C NMR spectra turn out to be undescriptive and are difficult to interpret [3, 4]. On the other hand, ^{27}Al NMR spectroscopy appears to be very useful and convenient method that allows easy establishing the nature of compounds, into which the cocatalyst transforms during the formation and functioning of the systems under consideration [5].

In this sense, the investigation of both already formed Ziegler system and the interaction of a cocatalyst with the transition metal complex and modifying additives, which are employed to improve the activity, productivity, and selectivity of Ziegler catalytic systems, is of particular interest. The report presents the data on possible application of the ^{27}Al NMR spectroscopy to study the formation and functioning of multicomponent catalytic systems is summarized on the example of nickel hydrogenation catalysts formed under the action of lithium aluminum hydride or alkoxyhydride aluminum derivatives.

The results presented in this report evidence that the ^{27}Al NMR spectroscopy can be an efficient tool for studying the dynamics of processes that occur during the formation and functioning of multicomponent (Ziegler) systems. Moreover, depending on the objective, this method can be the main one, while additional data can be obtained using other physical–chemical approaches, for example, IR, UV, EPR spectroscopy, gas evolution, mass spectrometry or GLC, TEM.

This work was supported by State Contract No. 1021051703316-6-1.4.3 of the Program of Fundamental Research.

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Machine learning application XANES analysis of Pd nanocatalysts

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Machine learning (ML) algorithms are a promising analytic tool that has found applications in many areas of science. This method has proven itself for tasks with a large number of parameters and is effective for big data processing. At the same time, near edge X-ray absorption spectroscopy (XANES) is a powerful tool widely used to determine the atomic and electronic properties of catalysts. However, XANES analysis has not completed procedure of analysis, since there is no unambiguous method for determining the structural parameters, while the amount of experimental data increases exponentially every day. We offered 2 options for solving this problem. On the one hand, in many cases, the analysis of XANES data requires the construction of theoretical models with a huge number of variable parameters. Application of ML to fit theoretical experimental data opens up new horizons for determining the structural parameters of the investigated substance. We applied the Extra Trees method for the time-resolved XANES spectra of Pd NPs. The evolution of structural parameters was obtained and compared with the method of principal component analysis (PCA) and multivariate parametric interpolation. We constructed a training set based on theoretical XANES spectra calculated in the FDMNES program for Pd NPs with different interatomic distances and in the presence of hydrogen and carbon-containing particles. On the other hand, it is used as an adjunct to extended-region X-ray absorption spectroscopy (EXAFS) analysis. We have labelled over 500 EXAFS spectra using a single-sphere analysis method. Then the Extra trees training was carried out for only XANES spectral regions, using tagged data. This approach made it possible to predict interatomic distances and the Debye - Waller parameter based only on experimental data.

The authors acknowledge the Ministry of Science and Higher Education of the Russian Federation for financial support (Agreement № 075-15-2021-1389 from 13.10.2021).

New evidence for the participation of Brønsted acid sites in perylene radical cation formation on borate-containing alumina catalysts by EPR spectroscopy of specifically adsorbed probe species

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Alumina [1] and anion-modified alumina [2] based catalysts have been widely used in catalytic processes requiring the presence of acid sites. An important characteristic of these catalysts is the concentration and ratio of Brønsted (BAS) and Lewis acid sites (LAS), which determines the yields and selectivity of target products formation in the most cases. Also, the problem of developing simple and experimentally convenient methods for studying the acid properties of catalysts under conditions as close as it possible to the real application are still relevant [1]. One of such methods can be EPR spectroscopy of probe molecules, in particular, the application of stable nitroxyl radicals, which form specific complexes with acid sites with the different shape of EPR spectra for each one [3]. Another approach is based on the adsorption of aromatic molecules (perylene, anthracene, etc.) on the surface of activated oxide supports or catalysts and quantitative analysis of paramagnetic species by EPR spectroscopy due to the formation of corresponding radical cations [2,4]. Despite a long time ago discovery of this phenomenon [4], an unambiguous mechanism and nature of active ionization sites have not yet been established.

Current work was aimed at studying the effect of B_2O_3–Al_2O_3 catalysts support composition in a wide range of modifier (0–30 wt.% of B_2O_3) content on the concentration and a ratio of BAS/LAS by probe EPR spectroscopy. Namely, is aimed at determining regularities in the influence of support acid properties on the ability to form EPR-detected radical cations after the adsorption of aromatic (perylene) probe molecule in order to confirm the hypothesis of the predominant participation of BAS in perylene ionization. To obtain more reliable results and correlations, we carried out additional studies of samples from a series of borate-modified alumina using ^{1}H MAS NMR and adsorption of nitroxyl 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) radical.

For the series of borate-modified alumina samples an increase in the concentration of BAS in the series with an increase in the boron oxide content to 30 wt.% was found according to probe EPR spectroscopy of TEMPO and solid state ^{1}H NMR [5]. Also, the results of determining BAS concentration directly via the concentration of TEMPO complexes with BAS are close in values to the concentration of perylene radical cations formed on the corresponding B_2O_3–Al_2O_3 samples. Thus, we can make an assumption, that BAS play the key role in the ionization of perylene to radical cations. The obtained results show that the proposed EPR approaches are promising for the quantitative analysis of surface BAS in the study of various acid solids, which confirmed by good agreement of our suggestion with the catalytic concepts of BAS concentration effect on the isomerization mechanism of hydrocarbons and deactivation of acid sites found out for the catalysts with different composition and structure [2,5].

This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the governmental order for Boreskov lnstitute of Catalysis (project AAAA-A21-121011890074-4).

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The optimal dynamic regime for CO oxidation on palladium nanocatalysts: insight from reinforcement learning

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In heterogeneous catalysis, researchers always strive to maximize the catalyst performance and increase the product yield. Many researchers are trying to improve the catalyst itself by changing its size, surface morphology, and composition or by modifying pressure, temperature, pH, etc. In past recent decades, oscillatory reactions based on perturbations of the catalytic system by extremal forces on gas/metal interfaces of catalysts have attracted a lot of attention and even largely formed new approaches to chemical engineering [1]. Here, the catalytic reaction is performed in some dynamically changed conditions using all benefits of transient kinetics.

However, a theory behind transition kinetics sometimes is not clear, and it is difficult to determine analytically or empirically an effective non-steady-state regime that realizes the full potential of the catalyst. One of the promising approaches is using the reinforcement learning (RL) approach to predict the best dynamic regime [2]. RL is the subfield of machine learning that studies how past data can be used to enhance the future manipulation of a dynamical system [3]. The agent (main character of RL) constantly gets some information from the environment and takes the action based on this information. This action in turn determines the further behavior of the environment, and the agent constantly receives a reward from the environment – the signal marking whether the actions of the agent lead to the desired result or not. Thus, the RL agent determines how to reach a goal in the best way (policy).

In this work, we performed optimization of parameters for CO oxidation reaction taking place on the surface of commercial Pd nanocatalysts (Pd/Al_2O_3, 5 wt.%, Chimet S.p.A) using the RL approach. First, we carried out several CO and O_2 cutoff and switching experiments at different temperatures (140 °C, 160 °C) analyzing reaction products by mass and Fourier-transformed infrared spectroscopies. Then, we approximated experimentally obtained CO_2 yields by a model of reaction and determined rate constants. Finally, we used refined kinetic equations to train the RL algorithm predicting the flows of reactants that leads to the highest production of CO_2. For this aim, we created the environment, which allowed our agent to set input flows of the CO and O_2. The agent could set the flows every 10 s of the episode lasting 500 s. We used the reward based on CO_2 output flow. Finally, using the model of the reaction simulating the catalyst deactivation, the agent learned the quasi-periodic policy of the flow switching. Selecting the policy gradient algorithm with continuous action space and extending observations to the flow rates on several successive steps we managed to obtain a set of nonstationary solutions. The maximal product yield was achieved for periodic variations of the gas flows ensuring a balance between available adsorption sites and concentration of activated intermediates.

As a result, we obtained improved periodic switching policies. Predicted dynamic regimes were validated by catalytic tests that demonstrated their supremacy over the steady-state regime.

This methodology opens a perspective for the optimization of relevant catalytic reactions under a non-stationary regime by rational use of reactants and varying conditions. The demonstrated approach can be expanded for optimization of many other industrially relevant reactions and catalytic systems.

The research was financially supported by the Ministry of Science and Higher Education of the Russian Federation (State assignment in the field of scientific activity, № 0852-2020-0019).

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In situ XPS and MS study of concentration hysteresis in hydrocarbon oxidation reactions over Pt, Pd and Rh-based catalysts

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Recently, it has been shown that methane oxidation over Pt/Al_2O_3 catalysts can proceed via two stable stationary regimes with low and high catalytic activity under identical external conditions [1]. It was found that the activity and selectivity of the platinum catalysts in a steady state depends greatly on the way of achieving the steady state. Using this hysteresis one can directly control the selectivity and activity of the platinum catalyst even with a low initial catalytic activity (e.g., at low temperature), improve the conversion from 10 to 90% level. For this purpose, oxygen concentration in the reaction mixture is decreased to a level less than $O_2:CH_4=1.5$ at the atmosphere pressure. It leads to certain increase in the methane conversion and selectivity. To achieve the maximum methane conversion (80-90%) the oxygen concentration in initial reaction mixture is then increased up to a ratio of $O_2:CH_4\leq2$.

Since this is new undescribed phenomenon, we had no literature data to elucidate reasons and to understand its nature. To establish the causes of this phenomenon, we studied the changes in the oxidation state of the active component in the real catalysts by *in situ* X-ray photoelectron spectroscopy (XPS).

In situ XPS experiments were carried out on a photoelectron spectrometer VGESCALAB "High Pressure", equipped with a special high-pressure cell and a quadrupole mass spectrometer with a two-stage differential pumping and high-precision mass flow-controllers. Experiments were conducted at constant hydrocarbon concentration (partial pressure of about 0.008 mbar) with varying the ratio of $O_2:CH_4$.

The Pt, Pd and Rh-based catalysts for the study were prepared via a wet impregnation of support (γ-Al_2O_3, SiO_2, TiO_2) with corresponding nitrate solutions followed by air-drying and calcination in air. The average size of supported particles was about 2 nm.

It should be noted that earlier studies of the hysteresis were conducted in laboratory reactors only at atmospheric pressure [1]. Therefore, there was no certainty that the experiment can be repeated at low pressures of about 0.01 mbar. However, our *in situ* XPS experiments under the conditions similar to those of the previous kinetic experiments at atmospheric pressure (ratio of the reactants and temperature) showed the presence of similar concentration hysteresis for all studied catalysts. Moreover, the concentration hysteresis is typical not only for the methane oxidation reaction, but also for propane oxidation. Study of the phenomenon included testing possible activity of the support (γ-Al_2O_3) and the in-situ cell in the reaction. The catalytic experiments showed that the pure support and *in situ* cell were not active in the reaction.

The *in situ* XPS spectra were recorded simultaneously with measurement of components concentrations by mass-spectrometry techniques. Analysis of XPS spectra showed that a transition of the catalyst to the active state occurs due to the reduction of the active component, and the subsequent transition to the low-active state is caused by its oxidation.

The *in situ* experiments allowed us to find out the cause of the new phenomenon of concentration hysteresis in the hydrocarbon oxidation over platinum group metal catalysts.

This work was conducted within the framework of budget project for Boreskov Institute of Catalysis.

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Decomposition of isopropylbenzene hydroperoxide, catalyzed by alkaline earth metal compounds

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The catalytic oxidation of hydrocarbons with molecular oxygen is one of the most important processes in petrochemical synthesis that underlies the industrial processing of hydrocarbon raw materials into valuable oxygen-containing products. A specific feature of the oxidation of alkylaromatic hydrocarbons (isopropylbenzene) is the production of hydroperoxides (intermediate products) as target products. The main consumer of isopropylbenzene hydroperoxide (IPBHP) is the large-scale production of phenol and acetone.

The traditional way to increase the selectivity of the hydroperoxides preparation processes is to search for various catalysts [1–3], the main place among which is occupied by compounds of non-transition metals, in particular, ethylhexanoates of alkaline earth metals (Mg, Ca, Sr, Ba). The undeniable advantages of ethylhexanoates are their low toxicity, availability, ease of preparation, and good solubility in hydrocarbons.

To establish the catalytic activity of group II metal compounds, we studied the catalytic decomposition of isopropylbenzene hydroperoxide in the presence of Mg, Ca, Sr, and Ba 2-ethylhexanoates. The patterns of catalytic decomposition of hydroperoxide were studied in the temperature range of 110–130 °C, $[\mathrm{IPBHP}]_0 = 0.5$ mol/l, $[\mathrm{Cat}]_0 = (0.1\text{–}7)\times10^{-3}$ mol/l.

All the studied compounds accelerate the decomposition of IPBHP, the catalytic effect decreases in the series: $\mathrm{Ca(EH)_2} > \mathrm{Mg(EH)_2} > \mathrm{Sr(EH)_2} > \mathrm{Ba(EH)_2}$.

It has been established that the decomposition of IPBHP is preceded by the formation of the hydroperoxide-catalyst intermediate. The kinetic proof of the formation of intermediate complexes is the “limitation” of the dependence of the hydroperoxide decomposition rate on its concentration at large $[\mathrm{IPBHP}]_0$. The stoichiometry of the complexes (1:1) was established, and the proposed 6-membered structure of the complex was considered. The kinetic, activation and thermodynamic parameters of the decomposition of isopropylbenzene hydroperoxide have been determined. The formation of intermediate complexes in the hydroperoxide-catalyst system was confirmed with a quantum-chemical method, the optimized structure was determined, and the stepwise mechanism of their formation and decomposition was established.

The research was carried out within the state task no. 075-00925-21-00 for 2020–2022 (scientific project “Catalysis in Oil Refining and Petrochemicals”, Research Funder is Ministry of Science and Higher Education of the Russian Federation).

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The effect of temperature on the synthesis of homogeneous molybdenum catalyst for the epoxidation of olefinic hydrocarbons

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The effect of temperature on the synthesis of a homogeneous molybdenum peroxide catalyst in the presence of isopropyl alcohol (IPAP) was studied [1]. The study of this parameter was carried out at temperatures from 45 ºC to 65 ºC.

Increasing the synthesis temperature from 45 ºC to 55 ºC allows not only to increase the process rate by 2 times (from $0.53\cdot10^{-4}$ to $1.1\cdot10^{-4}$ mol/(l·s)), but also to achieve a deeper conversion of molybdenum – 78.4%. Increasing the temperature by another ten degrees (65 ºC) makes it possible to increase the conversion (up to 86.4%), and, accordingly, the concentration of molybdenum in the solution up to 0.15 mol/l.

The constants for the reaction of molybdenum with hydrogen peroxide in the presence of a solvent, isopropyl alcohol, have been calculated. The activation energies were calculated from the temperature behavior of the initial rates of hydrogen peroxide consumption and Mo accumulation.

The research was carried out within the state task no. 075-00925-21-00 for 2020–2022 (scientific project "Catalysis in Oil Refining and Petrochemicals", Research Funder is Ministry of Science and Higher Education of the Russian Federation).

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Alloying bulk-immiscible elements at the nanoscale: an XPS/STM study of bimetallic Ag-Pt/HOPG nanoparticles

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The use of bimetallic catalysts is multifaceted, since adding a second component to catalytically active systems provides an ability to modify their stability, activity, and selectivity. The nature and ratio of metals on the surface of bimetallic catalysts directly affects the geometry of active sites and electronic properties of the active metal, so the preparation of bimetallic nanoparticles with a particular distribution of elements between surface and bulk plays a crucial role in catalyst design. There have been reported different types of mixing behaviour in bimetallic nanoparticles, ranging from structures with full or partial segregation of one element to nanoalloys with a nearly uniform distribution of both components within the entire particle volume [1]. Binary phase diagrams for bulk systems, routinely used for the prediction of alloy formation at the macroscopic scale, may not be appropriate for nanoparticles, since such systems comprise a significant number of atoms located at the surface and bimetallic interfaces what changes thermodynamic potentials governing the process of mixing. Thus, it may succeed when attempting to alloy bulk-immiscible elements at the nanoscale.

The Ag-Pt system represents a shining example of a solid having a large miscibility gap in the bulk. When referring to the nanoscale, both segregated and alloyed nanostructures are attainable depending on the synthesis route, temperature, initial ratio of metals, particle size, and other factors [2]. Getting more insight into these factors and their influence degree reveals great potential for deliberate tuning of surface structure in bimetallic nanoparticles since any reliable prediction model for this purpose is lacking to date. The present work reports the results of sequential thermal vacuum deposition of Ag and Pt atoms on the surface of a highly oriented pyrolytic graphite (HOPG) with the following stepwise thermal treatment of the prepared samples from room temperature up to 500 °C. Such a technique was previously succeeded in the preparation of different alloyed bimetallic nanoparticles, and the stage of annealing in ultrahigh vacuum played a key role in the formation of a regular alloy structure [3, 4]. In this study, two samples with different Ag/Pt surface atomic ratio (namely, 1.3 and 2.8) were prepared and characterized using X-ray photoelectron spectroscopy and scanning tunneling microscopy. In spite of a partial alloying already at the preparation stage, the bimetallic Ag-Pt/HOPG nanoparticles disintegrated into platinum oxide and silver monometallic nanoparticles after contact with air. Upon further heating in ultrahigh vacuum up to 350 °C, the partial formation of Ag-Pt alloy was observed, and the process of alloying was more pronounced in the sample which was initially 2.8-fold surface-enriched in silver. Interestingly, when heating the Ag-Pt/HOPG sample more depleted in Pt (Ag/Pt ~2.8) up to 350 °C without preceding contact with air, its transformation into alloy was complete. The Ag/Pt surface ratio changed weakly when alloying but abruptly dropped down to ~ 0.4 in both samples on further increasing the temperature to 500 °C, what indicated the disintegration of alloyed particles at this temperature followed by evaporation of Ag atoms from the solid phase.

This work was supported by the Russian Science Foundation (grant no. 19-13-00285-P).

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Influence of adsorption of electrically neutral reactants on electrical double layer in solid acid catalysts, and its relation to catalytic activity

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Among heterogeneous catalysts for cellulose hydrolysis much attention is given to oxidized and sulfonated carbon materials due to their high activity and stability. In oxidized carbons, organic acid sites (carboxyl and phenolic), are responsible for catalytic activity and involve in the adsorption of carbohydrates. In sulfonated carbons organic acid groups are present together with sulfonic acid groups [1]. At first glance, the presence of sulfonic groups could significantly enhance the catalytic activity, due to their higher acidity compared to carboxyl and phenolic ones. In addition, closely located organic and sulfonic groups, which jointly catalyze the hydrolysis of the glycosidic bond, probably have synergy [2, 3].

However, there appears to be no clarity in the literature regarding the efficiency of the catalysts sulfonation. In some cases, the increase in catalytic activity is moderate and the sulfonic groups seem to contribute less than organic ones (TOF decreases with the addition of sulfonic groups) [4]. In other cases, sulfonation significantly improves the catalytic efficiency and sulfonic groups contribute more to the process rate than organic ones (TOF increases with the addition of sulfonic groups) [5]. We suggest some insight regarding this issue in terms of solid acid dissociation and how it is affected by adsorption. Sulfonated carbons and other materials bearing strong acid groups form the electrical double layer in aqueous medium. This phenomenon is hardly discussed in studies of acid catalysis.

Adsorption isotherms of ethyl acetate and cellobiose on a mesoporous sulfonated carbon material at 295 K were obtained. The electrokinetic potential (ζ) of sulfonated carbon colloid was measured, showing -32.4 mV without adsorbate and generally decreased in absolute with the adsorption of both ether and carbohydrate. ζ noticeably increased at low concentration of adsorbates. The adsorbate fills narrow pores, displacing acidic protons, which accumulate near the outer surface, increasing the electrokinetic potential. The displacement of protons by adsorption going against electrostatic forces increases their thermodynamic activity. An increase in the adsorbate surface concentration leads to excessive thermodynamic activity of protons and subsequent suppression of the dissociation of acid groups. In the same way, cellulose hydrolysis products, especially oligosaccharides, can suppress the dissociation of the acid groups of sulfonated carbon catalysts. Considering the discrepancy in the earlier studies [4, 5] we suggest an explanation regarding the catalytic activity of sulfonated carbon catalysts in cellulose hydrolysis: catalysts with a larger surface area could be more efficient in producing glucose.

Catalytic activity is associated with a lower probability of sulfonic groups dissociation suppression caused by the adsorption of oligomers.

This research was carried out with financing by a Grant from Russian Science Foundation (Project No. 21-73-20269).

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Inorganic tetranuclear catalyst for water oxidation in artificial photosynthesis

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In connection with environmental problems, the 21st century will be the century of transition from hydrocarbon energy to other types of energy carriers, so the search for new alternative energy sources becomes very important. Solar energy is one of the alternatives. Artificial photosynthesis (**AP**) – the decomposition of water into O_2 and H_2 - is a way to convert solar cells. $P680^+$ radical cations are the oxidizing agents in oxygenic photosynthesis, and a manganese cofactor (Mn_4CaO_5) is the catalyst. In its coordination sphere one O_2 molecule is formed according to the reaction: $4\ P680^+ + 2\ H_2O = 4\ P680 + O_2 + 4\ H^+$.

In the AP clusters of other transition metals are used for this purpose, including ruthenium. Ruthenium polynuclear complexes are of interest as promising highly efficient catalysts for water oxidation in artificial photosynthesis with the aim of creating photocatalytic converters of solar energy into chemical fuel energy in the future. These earlн catalysts haв low activity due to the presence of organic ligands, which are more easily oxidized than water, and also contain labile Ru–O–Ru bonds, which lead to catalyst deactivation. Our scientific group synthesized a tetranuclear complex of ruthenium with polyoxotungstate ligands and Li^+ countercation $Li_{10}[\{Ru_4(\mu\text{-}O)_4(\mu\text{-}OH)_2(H_2O)_4\}(\gamma\text{-}SiW_{10}O_{36})_2\}]\cdot 25H_2O$ ($Li_{10}Ru_4$) and it was compared with the complex with $Rb_8K_2Ru_4$. The complex was characterized by IR and Raman spectroscopy. The peak at 800 cm^{-1} corresponds to the polyoxtungstate region, and the peak at 483 cm^{-1} corresponds to symmetrical Ru-O-Ru vibrations. The preservation of the structure of $Li_{10}Ru_4$ in aqueous solution is confirmed by the ESI-mass-spectrum (*m/z* = 1798 and *m/z* = 1348 correspond to $[H_9Ru_4Si_2W_{20}O_{78}]^{3-}$ and $[H_8Ru_4Si_2W_{20}O_{78}]_{4-}$ ions containing a tetraruthenium core after the loss four molecules of H_2O. At 400 °C the adamantane-like catalyst core $[H_2O\cdot Ru_4O_6 + 2H]^-$ with *m/z* = 521 is retained. An analysis of the CVA curves of $Li_{10}Ru_4$ and $Rb_8K_2Ru_4$ showed that $E_{1/2}$ for $Li_{10}Ru_4$ is higher than that for $Rb_8K_2Ru_4$ (1013 and 973 mV). The photocatalytic oxidation of water in the $Li_{10}Ru_4$ – bpy_3RuCl_2 – $K_2S_2O_8$ system as a function of the [$Li_{10}Ru_4$] has been studied. The rate of formation of O_2 is high (number of catalyst turnovers TON = 475, yield of O_2 in 2 h Q = 0.92, quantum yield of O_2 Φ = 0.29) and was compared to $Rb_8K_2Ru_4$ (180, 0.41, 0.09, respectively). A reaction mechanism has been proposed.

The methodology for the kinetic study of the reaction of the 2-methylimidazole formation by NMR-spectroscopy *in situ*

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Imidazole and its derivatives are commonly used in every aspect of life. Of particular interest from imidazole derivatives is 2-methylimidazole [1]. This compound is used as a raw material in the synthesis of medicines, polymers, insecticides and dyes, and is an accelerator for curing epoxy resins.

The main method of obtaining 2-methylimidazole is the condensation of glyoxal, acetaldehyde and ammonia (Debu method), occurring in an aqueous solution [2]. Despite the large studies in the chemistry of imidazoles, a systematic study of the kinetics of their formation from the point of view of the nature of the reagents used and factors affecting the rate of formation and composition of the final mixture has not been carried out to date, and the kinetic parameters of this reaction have not been established.

The development of methodological approaches for experimental investigation of the kinetics of the interaction of acetaldehyde and glyoxal with ammonia is an important area of modern physical organic chemistry and chemical industry.

Thereby, this work was focused on the development of a methodology for determining the kinetic parameters of the reaction of the formation of 2-methylimidazole during condensation of acetaldehyde, glyoxal and ammonia in an aqueous solution. The acetaldehyde and ammonia adduct (acetaldehyde-ammonia trimer) [3] as the synthetic equivalent of acetaldehyde and ammonia in reaction with glyoxal and NMR spectroscopy in situ [4] were used. The developed method for determining kinetic parameters allows us to establish the reaction order, rate constants, initial rates of product formation and reagent consumption.

The three-necked flask containing a reflux condenser and a thermometer was used for the experiment. Glyoxal and an acetaldehyde-ammonia trimer with a molar concentration of 0.6 mol/l were introduced into the flask. (in ratio 1:1). The time of addition of glyoxal was noted as the reaction start time. Further, a sample from the reaction flask was taken and transferred to an ampoule with D_2O and an internal standard – DMSO. After that, the ampoule was placed in an NMR spectrometer and the spectra were monitored in progress of the reaction.

For the first time to establish the main kinetic parameters (rate constant was $0.8\cdot10^{-3}$ s^{-1}, initial product formation rate was $0.83\cdot10^{-4}$ $mol\cdot l^{-1}\cdot s^{-1}$, reagent flow rate was $1.14\cdot10^{-4}$ $mol\cdot l^{-1}\cdot s^{-1}$ and order of a reaction 1). The developed in situ NMR technique for monitoring the concentrations of reagents and reaction products in real time has been applied for the first time for this class of reactions. The developed in situ NMR method was used for the first time in this class of reactions to monitor concentrations of reactants and reaction products. The proposed method can also be used to establish the kinetic parameters of similar organic reactions occurring in solution.

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Aggregate state transformation in the near-surface area

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In recent years, the field of catalysis associated with the thin layers has been actively developed. Mainly, leaching layers are studied, the sizes of which can vary from nanoparticles to molecular clusters, where the nature of the most active catalytic particles can differ significantly from the initial form. It has been repeatedly noted that in many catalytic reactions used in organic synthesis, the dynamically available and most active form of the catalyst is still undiscovered. So far, no unifying concepts have been developed to incorporate dynamic behavior into catalytic cycles, although it has already become clear that there is nothing static in catalysis. In a number of gas-liquid organic systems of the substituted methanes, ethanes and aromatics (CCl_4, $CHCl_3$, CH_2Cl_2, CH_3I, CH_3NO_2, CH_3CN, CH_3OH, $C_2H_4Cl_2$, $C_2H_3Cl_3$, $C_2H_2Cl_4$, C_6H_6, C_4H_4O, C_4H_4S), on the other hand, in thin intermediate layers near a solid surface, a transformation of the aggregate state can occur, accompanied by structural rearrangements and leading to the manifestation of a certain transitional phase state, which represents an activated form of a substance with mixed gas-liquid properties, resembling a fluid, which no longer requires the presence of a third-party catalytic factor [1].

As further studies showed, the phenomenon of thin layers is applicable not only to gas-liquid organic systems, but also to the liquid substituted silanes ($SiCl_4$, $SiHCl_3$, SiH_2Cl_2), which, being deposited on a solid surface in an atmosphere of dried argon, can form a solid silicon dioxide film on the surface due to mild oxidation, under which liquid is retained in a thin layer. Once the layer is finally encapsulated, silanes can survive for long periods of time in atmospheric humid air, exhibiting unusual resistance to hydrolysis. In this case, the effect is opposite to that discussed above for organic systems - the component is not activated, but, on the contrary, is deactivated, which makes it possible to conduct direct oxidation of silanes in order to obtain silicon dioxide, which is of great practical importance for catalysis. Subsequently, it can be used as a supported material for the heterogenous catalysis with ionic liquids followed by an injection of the active nanoparticle component, called “supported ionic liquid phase” or “supported ionic liquid catalyst”, through physical adsorption or covalent binding to the ionic liquids on the surface. One of the most valuable observations in the course of this experiment was that the encapsulated thin-layer liquid undergoes significant aggregate state transformation for a long time (about a month), which confirms the possibility of such transitions in the near-surface area not only for organic systems. The results included both IR spectral data and electron microscopy [2].

In addition to the experimental studies described above, theoretical calculations were also conducted using the DFT modeling method (for CCl_4, $CHCl_3$, $CDCl_3$, $CHBr_3$, CH_2Cl_2, CH_3I, CH_3NO_2, CH_3CN, C_6H_6, C_6D_6, C_6F_6). As has been shown, the formation of the organic compounds’ liquid phase is a complex multistage process involving many factors, such as intermolecular binding. It seems likely that the observed aggregate state transformation in the near-surface area, leading to the formation of a transitional fluid, is one of the process stages. However, the proposed methods make it possible to conserve this transitional and normally unstable state in the thin layers for a long time that allows a new-level study of the liquid phase nature for practically and technologically important organic substances [3].

This work was supported by the Ministry of Science and Higher Education of the Russian Federation in the Framework of the Basic Part of the State Task (theme FSWE-2020-0008 project 0728-2020-0008). The equipment of the Ural Center for Shared Use “Modern Nanotechnology” UrFU was used.

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Operando XRD study of Mn-Zr oxide catalysts in CO and C_3H_8 oxidation reactions

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Transition metal catalysts are of particular interest due to their low cost, high stability, and resistance to catalyst poisons. Mn-based oxide catalysts are among the most promising transition metal catalysts. The catalytic properties of manganese oxides depend on the process conditions, in particular, on the composition of the fuel used. Therefore, the properties of Mn-containing oxides under various conditions of the CO oxidation and C_3H_8 were studied via in situ X-ray diffraction and mass spectrometry.

Catalysts with a ratio of cations Mn:Zr = 3:7 were obtained by coprecipitation and calcination at the temperatures of 400–800°C. The samples were characterized by XRD, N_2 adsorption, TPR and XPS. The most active catalyst was calcined at the temperature 650 °C and it consisted of 97% $Mn_yZr_{1-y}O_{2-\delta}$, 3% Mn_2O_3. Its activity is high due to the partial decomposition of the $Mn_yZr_{1-y}O_{2-\delta}$ solid solution and the formation of highly dispersed manganese oxide particles on the surface.

For the most active catalyst in situ XRD experiments were carried out under the conditions of the propane oxidation reaction ($C_3H_8+O_2$), and for comparison in O_2 and C_3H_8. The catalyst was stable under conditions of O_2 presence and its phase composition was constant. In the C_3H_8 environment the reduction of Mn ions in $Mn_yZr_{1-y}O_{2-\delta}$ structure was observed, as well as the reduction of Mn_2O_3 to MnO.

A mixed Mn-Zr catalyst with the ratio Mn:Zr = 6:4 was obtained by coprecipitation and calcination at the temperature 650°C. It was characterized by XRD and TEM methods. Phase composition of the catalyst was 72% $Mn_yZr_{1-y}O_{2-\delta}$, 18% Mn_2O_3, 10% Mn_3O_4. A catalytic test has shown the increase of CO conversion after redox cycle addition from 25 to 40%. Operando XRD experiment under conditions of CO oxidation was carried out with different treatments of the catalysts. The first treatment was the reduction in 5% CO with further reoxidation and it showed the conversion increase from 21 to 42% and partial reduction of Mn oxides to MnO. The second treatment was the reduction in 10% CO that led to the total MnO_x reduction to MnO. After that CO conversion increased to 71%. Thus, redox cycles caused a segregation of highly dispersed Mn_3O_4 particles at the surface that increased a catalytic activity.

This work was supported by the Russian Science Foundation, project 21-73-10218.

Electronic and optical properties of Ti-doped bismuth metasilicate

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Renewable energy sources have gained research interest for decades. Solar energy catalysis is considered to be one of safe and sustainable alternatives to fossil fuel. There are a few Bi-based materials with promising photocatalytic properties. Though being promising photocatalysts, bismuth silicates are less investigated comparing to other bismuth compounds. Bismuth metasilicate Bi_2SiO_5 is of a particular research interest due to its perovskite-like structure and higher photocatalytic activity. Recently, Ti-doped structures of Bi_2SiO_5 were synthesized with titanium content up to 0.5. In present work, their electronic and optical properties were studied by means of density functional theory.

Calculations were performed using OpenMX quantum chemical package. PBE exchange-correlation functional and standard recommended PAO and VPS settings were used. The Mönkhorst-Pack scheme was implemented for k-point Brilloin zone sampling. 1×6×6 *k*-point mesh was used for geometry optimization according to bismuth metasilicate unit cell size while the number of *k*-points was doubled in each direction for DOS calculations.

First, Bi_2SiO_5 unit cell was optimized. Lattice parameters were found to be in good agreement with experimental data [1]. Then, $Bi_2Si_{0.75}Ti_{0.25}O_5$ and $Bi_2Si_{0.5}Ti_{0.5}O_5$ structures were modeled by replacing one or two silicon atoms with titanium. Less than 1.5% lattice expansion is observed for $Bi_2Si_{0.75}Ti_{0.25}O_5$ with respect to original structure, and 1.6–2.7% expansion depending on the direction is observed for $Bi_2Si_{0.5}Ti_{0.5}O_5$.

Band structure of the doped bismuth metasilicates preserves nature of their counterpart, being direct semiconductor. Band gap slightly decreases when Ti is introduced in structure. However, it doesn't change much as its concentration increases. PDOS analysis shows that titanium states mostly contribute to the bottom of the conduction band. Optical absorption edge shifts from 511 nm for pristine Bi_2SiO_5 to 557 nm for both doped compounds.

This work was supported by Russian Science Foundation, grant no. 19-73-30026.

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Transform in situ DRIFTS of hydride Pd nanoparticles to quantitative tool for structure characterization

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Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is widely used for qualitative in situ characterization of catalysts [1]. Since it is sensitive to the molecules adsorbed on the surface of the catalyst, it is usually applied to examine the reactivity of surface species by a probe molecule such as CO. In this work, we suggest a technique to extract structural parameters of the bulk, namely Pd-Pd interatomic distances and H/Pd ratio, of the catalyst from DRIFTS data. For this, series of DRIFTS and X-ray absorption spectroscopy (XAS) spectra were collected during the formation of palladium hydride phase formation in presence of CO. Then the database of the key features of IR spectra was constructed and correlated with the results of XAS data analysis and supportive density functional theory (DFT) calculations. Then machine learning algorithms [2] were used to identify the most representative descriptors such as bridge peak position.

The authors acknowledge the Ministry of Science and Higher Education of the Russian Federation for financial support (Agreement № 075-15-2021-1363).

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Aerogel calcium aluminates: synthesis and investigation of surface active sites

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For a long time, oxide systems based on calcium aluminates (CA) of different stoichiometry are used in the composition of cements, ceramics and other composite materials. The conventional preparation method for CA materials is the calcination of the corresponding oxides taken in an appropriate ratio at high temperatures up to 1550 °C [1]. Among the low-temperature preparation techniques, an interaction of aluminum and calcium salts solutions at 80 °C should be mentioned. The thermal treatment (drying at 120 °C and calcination at 1100 °C) of the obtained gel gives the CA material with specific surface area of 3.3 m^2/g [2–3].

In the present work, a series of CA samples ($CaO{\cdot}Al_2O_3$, $12CaO{\cdot}7Al_2O_3$, and $3CaO{\cdot}Al_2O_3$) was synthesized via the aerogel technique [4]. At the first stage, calcium metal was mixed with methanol and heated with a backflow condenser at 70 °C for 1 h. Then, an appropriate amount of aluminum isopropoxide was added to the formed solution of calcium methoxide along with isopropanol and toluene. The mixture was stirred without heating for 1 h. Finally, hydrolysis of the mixture by distilled water was performed. On the following day, the formed gel was dried in an autoclave in the argon atmosphere for 3 h with the heating up to 265 °C and the corresponding pressure increase to 80 atm. The dried samples were calcined in a muffle furnace at 500 °C. This technique is known to yield materials with high surface area and porosity.

Obtained CA aerogels were characterized by the low-temperature nitrogen adsorption. The specific surface area values of as-prepared $CaO{\cdot}Al_2O_3$, $12CaO{\cdot}7Al_2O_3$, and $3CaO{\cdot}Al_2O_3$ aerogels were as high as 513, 327, and 265 m^2/g, correspondingly. The calcination of the samples at 500 °C resulted in the reduction of surface area in 1.6-1.8 times.

The EPR spectroscopy using spin probes was applied to analyze the active sites on the surface of the CA aerogels. Calcium aluminate aerogels calcined at 500 °C were shown to have electron-donor sites capable of ionizing 1,3,5-trinitrobenzene (TNB) similar to those present on the Al_2O_3 surface. The concentration of electron-donor sites over the calcium aluminate aerogels tested using TNB significantly increased (from $0.28{\times}10^{18}$ to 1.12×10^{18} g^{-1}) with an increase of the calcium concentration in the sample despite the surface area decrease in this sequence.

Significant concentrations of electron-acceptor sites capable of forming radical cations after adsorption of phenothiazine were observed over the aerogels after calcination at 500 °C. The concentration of the radical cations formed from phenothiazine was found to decrease (from $6.13{\times}10^{18}$ to 2.28×10^{18} g^{-1}) with an increase of the Ca:Al ratio in the aerogels. This trend was opposite to the one observed for the concentrations of electron-donor sites.

Unique for mayenite is the formation of nitroxyl radicals from diphenylamine. Their formation indicates that active O^- or peroxyl radicals are present on the surface of calcium aluminate aerogels. The total intensity of the spectra increased by a factor of 3 with the decrease of the Ca/Al ratio going from 1.14×10^{18} g^{-1} for $3CaO{\cdot}Al_2O_3$ to $3.38{\times}10^{18}$ for $CaO{\cdot}Al_2O_3$. However, the contribution of the triplet attributed to surface diphenyl nitroxide radicals is markedly higher over $3CaO{\cdot}Al_2O_3$ than over the other samples.

Calcium aluminates with various stoichiometry with high surface area were synthesized by aerogel method. Active electron-donor, electron-acceptor, radical sites characterized by EPR using spin-probes were observed on their surface. These materials are promising for future using as catalysts supports.

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Machine-learned classification for zeolite frameworks supplemented by their simulated infrared spectra

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There are a lot of zeolite structures that have proven themselves as catalysts in various important industrial reactions. However, permanent development of industrial procedures, improvements of applied techniques and optimization of catalytic processes requires further study of zeolite structures.

Infrared spectroscopy is one of the most accessible qualitative methods determines what types of bonds, functional groups and structural units are present in the material. We wondered if this method could be improved to extract more information about the structure of the zeolite. The aim of this project is to classify the vibrational modes of zeolites by the type of structural units of zeolites, so called natural tiling [1], and to establish the dependences of their frequencies on structural parameters using theoretical calculations from first principles.

In order to classify the existing structures of zeolites by their structural elements, K-Means clustering was applied using python code. Framework structures for more than 50 different types of marked samples were used in the Vienna ab initio Simulation Package (VASP) version 5.3 [2] for its structural optimization with further computation of vibrational spectra. Optimization process included 5 steps with sequential optimization of ions positions and cell volume. For calculations of vibrational spectra, only the Γ point was considered. Periodic DFT calculations were performed with a 500 eV cutoff energy, a plane-wave basis, and the PBE functional. Electron-ion interactions were described with projector augmented wave (PAW) method [3]. Theoretical IR spectra were compared with the experimental ones from KnowItAll and RUFF databases.

Thus, based on collected data, previous studies, and machine learning algorithms correlations of the positions of vibrational frequencies on the structural parameters (angles and bond lengths) of zeolite units were established. The results obtained has a fundamental scientific importance, since the methods developing can be applied to vibrational spectra to extract structural parameters. On the other hand, this technique will significantly increase the information content of infrared spectra, which is of great practical importance and can be applied to a wide range of objects.

This work was supported by Russian Science Foundation Grant # 22-23-01007.

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SECTION 4

INDUSTRIAL IMPLEMENTATION OF CATALYTIC PROCESSES

Deactivation and regeneration of hybrid cobalt Fischer-Tropsch synthesis catalyst

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The Fisher-Tropsch (FTS) synthesis is a key stage in the technology for producing synthetic oil and high-quality fuel components from carbonaceous raw materials: natural gas or associated petroleum gas, coal, and biogas. Deactivation of FTS catalyst is an impotent problem for industrial application of this process. It affects catalytic activity, decreases the selectivity to C_{5+} hydrocarbons, and increases the selectivity to methane and hydrocarbons C_2-C_4. The interest of modern researchers is to investigate the reasons for deactivation and search for solutions to inhibit the deactivation and develop efficient methods to regenerate the Fisher-Tropsch catalyst.

The Fisher-Tropsch synthesis is a high exothermic process. Local catalyst overheating causes carbon deposition which is an important reason for deactivation. The introduction of the heat-conductive additive: aluminum metal powder or exfoliated graphite into the catalyst can help to gain high thermal conductivity of the catalyst and decrease catalyst local overheating [1].

Another important reason for deactivation is the blocking of the catalyst surface by heavy waxes. The introduction of zeolites into catalysts results in cracking heavy hydrocarbons into light oil [2]. Catalysts comprising both a Fischer–Tropsch active metal and a zeolite component called hybrid catalysts.

Several methods of regeneration of deactivated Fisher-Tropsch catalyst were described in the paper [3].

The aim of this work is to measure of deactivation rate in long run and develop the optimal methodology for regeneration of hybrid cobalt-based Fisher-Tropsch catalyst. The supports were prepared by mixing heat-conductive component, H-Beta zeolite, and boehmite as a binder. Catalyst support pellets had a 1.5 mm diameter and 3–5 mm length. All catalysts were prepared by two-step incipient wetness impregnation of supports with water solution of $Co(NO_3)_2 \cdot 6H_2O$, every step was followed by calcination in air flow. Cobalt loading was 20 wt.% calculated on support weight.

The long run test was in a tube shell double pipe ("pipe-in-pipe") type reactor with a diameter of the inner tube of 12 mm. and 6000mm in length. The deactivation rate during 3000 hours of the run was 13%, from 53 to 46 μmol/(s×g Co). The deactivation rate of the tested catalyst was much lower than was shown in other investigations were 50% activity lost during 1300–1900 hours run.

In this investigation, we tried several methods of regeneration catalyst after a long run. The optimal method includes 2 steps: oxidation of catalyst at 450 °C in diluted air flow with O_2 content from 3 to 21% and reduction of catalyst in hydrogen flow at 350–370 °C on the activation step. 98% of the activity of the hybrid Fisher-Tropsch catalyst was recovered.

To sum up, it was shown that the hybrid cobalt Fisher-Tropsch catalyst lost 13% of its activity during 3000 hours long test run. Also, an efficient method of regeneration of deactivated catalyst was tested which recovered 98% of activity.

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Synthesis of beta-propiolactone by *in situ* catalytic interaction of formaldehyde with ketene

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COVID-19 (coronavirus infection 2019) is a potentially severe acute respiratory infection caused by the SARS-CoV-2 coronavirus. The most effective method to combat COVID-19 is vaccination. Currently, a number of vaccines have been developed to prevent COVID-19, among which a special place is occupied by the inactivated vaccines, which are obtained by chemical inactivation of the virus. An important condition for the effectiveness of vaccines is the choice of the inactivator and optimal conditions for inactivation, which makes it possible to deprive the virus of infectivity while maintaining its immunogenic properties in a maximal degree.

In the practice of developing inactivated vaccines the most widely used are chemical inactivators applied in the production of licensed viral vaccines. The choice of inactivation method is based on the mechanism of action of the inactivator and the properties of the virus to be inactivated.

Beta-propiolactone is a promising inactivator of COVID-19 featuring the strongest biocidal effect. The effectiveness of beta-propiolactone is associated with the complete destruction of the virus RNA within a maximum of two days, while inactivation occurs under physiological conditions, i.e. without temperature rise. Currently, despite the high demand for beta-propiolactone, it is not produced in Russia. At the same time, the market value of 1 kg of beta-propiolactone costs about 100 thousand rubles. Pharmaceutical companies and research centers are forced to purchase imported reagents for research and development of vaccines. In this regard, the need to develop a domestic technology for the production of beta-propiolactone is of particular relevance.

We have developed a laboratory method to synthesize beta-propiolactone by catalytic interaction of formaldehyde with ketene generated *in situ*. $BF_3O(C_2H_5)_2$, $AlCl_3$, $ZnCl_2$ and their mixtures in various ratios were chosen as the catalyst. It was shown that the use of catalyst mixtures significantly increases the yield of beta-propiolactone compared to individual ones. The developed method makes it possible to obtain a product with a purity of up to 98%.

This study was supported by the Tomsk State University Development Programme (Priority-2030).

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Scientific edition

CATALYSIS: FROM SCIENCE TO INDUSTRY

Proceedings of
VII International scientific school-conference for young scientists

2022, October 11–15

Original layout by *T.S. Kharlamova*
Cover designed by *O.V. Kireeva*

It's published at TSU Publishing House as provided by original layout

Signed to print 10.10.2022. Format $60 \times 84_{1/8}$. Offset paper
№1. Offset print. Printed sheets 22,1.
Order №5163. Number of copies 500 issues.

ISBN 978-5-907572-26-3

9 785907 572263 >