CATALYSIS:
from science to industry

PROCEEDINGS OF VIII INTERNATIONAL SCIENTIFIC SCHOOL-CONFERENCE FOR YOUNG SCIENTISTS

30 September - 3 October, 2024
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
VIII International scientific school-conference for young scientists

September 30 - October 3, 2024

Tomsk 2024

UDC 544.47/544.72+661.7
LBC 24.54
C30

C30 **Catalysis: from science to industry:** Proceedings of VIII International scientific school-conference for young scientists “Catalysis: from science to industry” / Tomsk State University. – Tomsk: TSU Publishing House, 2024. – 122 p.

ISBN 978-5-907722-99-6

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

UDC 544.47/544.72+661.7
LBC 24.54

VIII INTERNATIONAL SCIENTIFIC SCHOOL-CONFERENCE FOR YOUNG SCIENTISTS

“CATALYSIS: FROM SCIENCE TO INDUSTRY”

ORGANIZERS

National Research Tomsk State University

PARTNERS AND SPONSORS

“Engineering chemical and technological centre” Ltd., Tomsk

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”

The event is held within the framework of a subsidy from the federal budget to higher education organizations to implement the events aimed at supporting student scientific communities

INFORMATION SUPPORT

Journal “Kinetics and Catalysis”

SCIENTIFIC COMMITTEE

Chairperson:
Vodyankina O.V., Tomsk State University, Tomsk, Russia

Members:
Lavrenov A.V., Center of New Chemical Technologies BIC SB RAS, Omsk, Russia
Taran O.P., Institute of Chemistry and Chemical Technology SB RAS, Krasnoyarsk, Russia
Vosmerikov A.V., Institute Petroleum Chemistry SB RAS, Tomsk, Russia
Sadykov V.A., Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
Knyazev A.S., Tomsk State University, Tomsk, Russia
Kholdeeva O.A., Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
Gordeeva L.G., Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
Boronin A.I., Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
Kulinich S.A., Research Institute of Science & Technology, Tokai University, Kanagawa, Japan
Zvereva I.A., St. Petersburg State University, St. Petersburg, Russia
Rostovshchikova T.N., Lomonosov Moscow State University, Moscow, Russia
Lokteva E.S., Lomonosov Moscow State University, Moscow, Russia
Kozlova E.A., Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
Yakhvarov D.G., Kazan Federal University, Kazan, Russia
Svetlichnyi V.A., Tomsk State University, Tomsk, Russia

ORGANIZING COMMITTEE

Chairperson:
Kharlamova T.S., Tomsk State University, Tomsk, Russia
Secretary:
Tuguldurova V.P., Tomsk State University, Tomsk, Russia

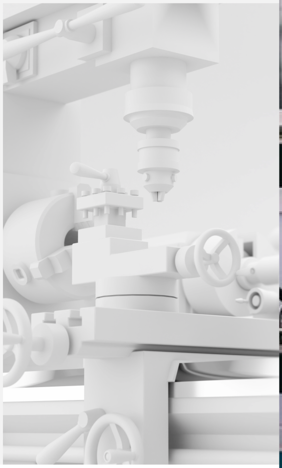
Members:
Belik Y.A., Tomsk State University, Tomsk, Russia
Bugrova T.A., Tomsk State University, Tomsk, Russia
Blinov E.D., Tomsk State University, Tomsk, Russia
Evdokimova E.V., Tomsk State University, Tomsk, Russia
Fakhrutdinova E.D., Tomsk State University, Tomsk, Rossia
Grabchenko M.V., Tomsk State University, Tomsk, Russia
Kotov A.V., Tomsk State University, Tomsk, Russia
L'vova E.S., Tomsk State University, Tomsk, Russia
Magaev O.V., Tomsk State University, Tomsk, Russia
Nikulaichev S., Tomsk State University, Tomsk, Russia
Putanenko P.K., Tomsk State University, Tomsk, Russia
Reutova O.A., Tomsk State University, Tomsk, Russia
Salaev M.A., Tomsk State University, Tomsk, Russia
Salaeva A.A., Tomsk State University, Tomsk, Russia
Savel’eva A.S., Tomsk State University, Tomsk, Russia
Timofeev K.L., Tomsk State University, Tomsk, Russia
Zubkov A.V., Tomsk State University, Tomsk, Russia

SPONSOR/PARTNER PRESENTATIONS

Центр малотоннажной химии

на территории Промышленного парка Томской области

- парк опытно-промышленных химических установок
- малотоннажные химические производства
- эксплуатационный блок
- корпус особо чистой химии для радиоэлектроники
- корпус работы с прекурсорами



5

га, площадь проектируемого парка

1

млрд ₽, инвестиции в проект

ect-center.com

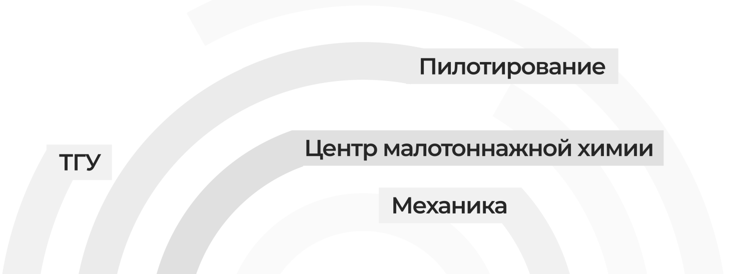
ect-m.com

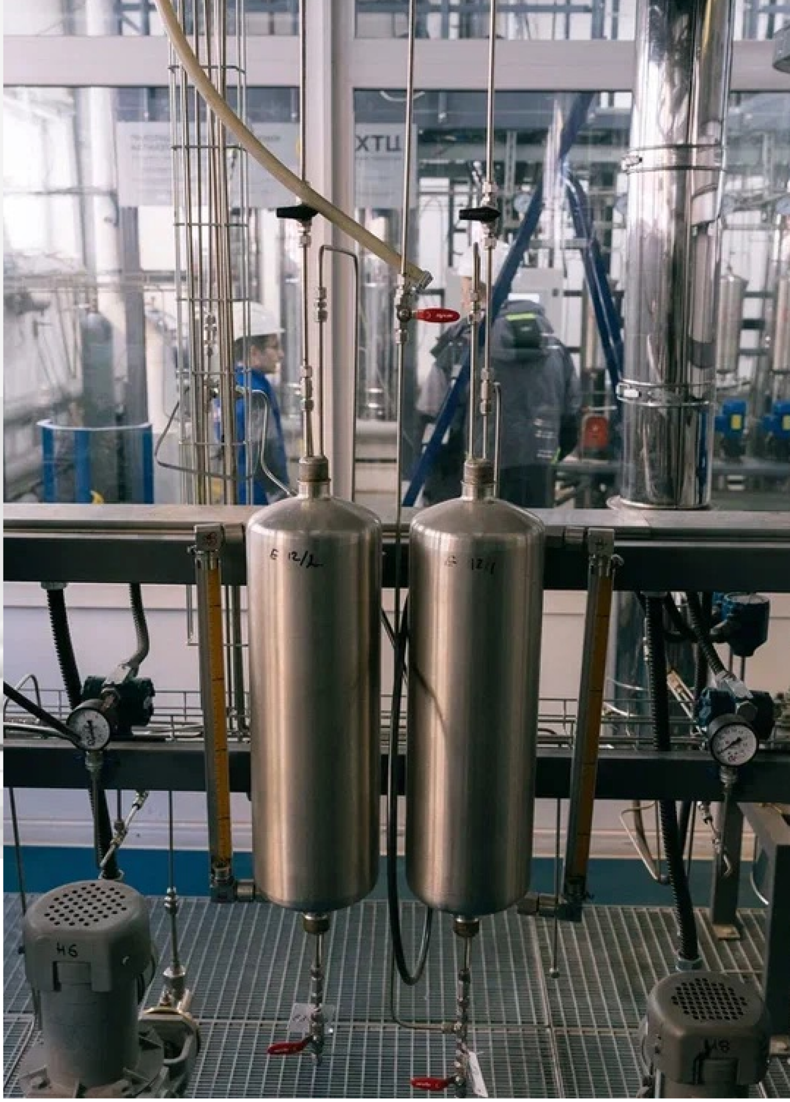
Томск
Московский тракт, 57
+7 (3822) 909-969

Новосибирск
ул. Мусы Джалиля, д. 13, оф. 1
+7 (383) 373-20-43

Екатеринбург
ул. Карла Либкнехта, 22

Санкт-Петербург
ул. Марата, 47-49, оф. 700





ИХТЦ

Эффективное решение инжиниринговых задач

для химической промышленности

Инжиниринговый химико-технологический центр

- продвинутая аналитика
- научно-исследовательские работы
- сопровождение бизнес-проектов
- масштабирование химических технологий
- создание и запуск химических производств
- создание опытно-промышленных установок

ИХТЦ
МЕХАНИКА

Изготовление уникального комплексного оборудования для химических производств и лабораторий

лабораторные, опытно-промышленные установки, стенды, реакторы, автоклавы, комплектующие и арматура из разных материалов, включая специальные сплавы и стекло, по индивидуальным требованиям заказчика

Разработка собственных технических решений для последующей реализации

КИПиА, отдельные узлы реакторного оборудования и т. п.

Конструкторский отдел и собственное механическое производство

ИХТЦ обеспечивает комплексный процесс внедрения химических технологий

С 2017 года ИХТЦ регулярно входит в тройку лучших инжиниринговых центров России по рейтингу НТИ РФ

150+ специалистов в команде	**40+** проектов в работе
10+ малотоннажных производств ежегодно	**3** производственные площадки

ИХТЦ
ПИЛОТИРОВАНИЕ

- Создание и эксплуатация пилотных установок, строительно-монтажные и пусконаладочные работы
- Авторское сопровождение организации химических производств
- Подбор оборудования для новых технологических процессов
- Оптимизация технологических схем
- Масштабирование химических технологий

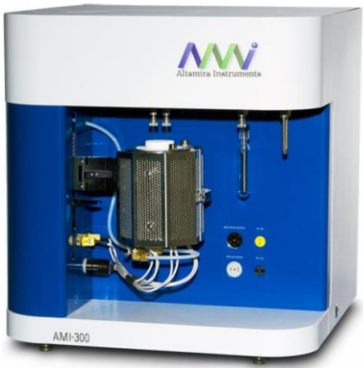
ЛАБТЕСТ
LABTEST

ЛАБТЕСТ

НАДЕЖНЫЙ ПОСТАВЩИК АНАЛИТИЧЕСКОГО
ОБОРУДОВАНИЯ И КОМПЛЕКТУЮЩИХ

www.lab-test.ru
info@lab-test.ru
+7495-256-24-84

*Компания **«НКЦ «ЛАБТЕСТ»** является официальным представителем **«Altamira Instruments»** и предлагает широкий спектр газо-адсорбционного оборудования.*



АДСОРБЦИОННОЕ ОБОРУДОВАНИЕ

для исследования микро- и мезопористых материалов.

- ✓ Анализаторы удельной поверхности и пористости;
- ✓ Анализаторы газовой сорбции под высоким давлением;
- ✓ Анализаторы сорбционной емкости и кривых прорыва.

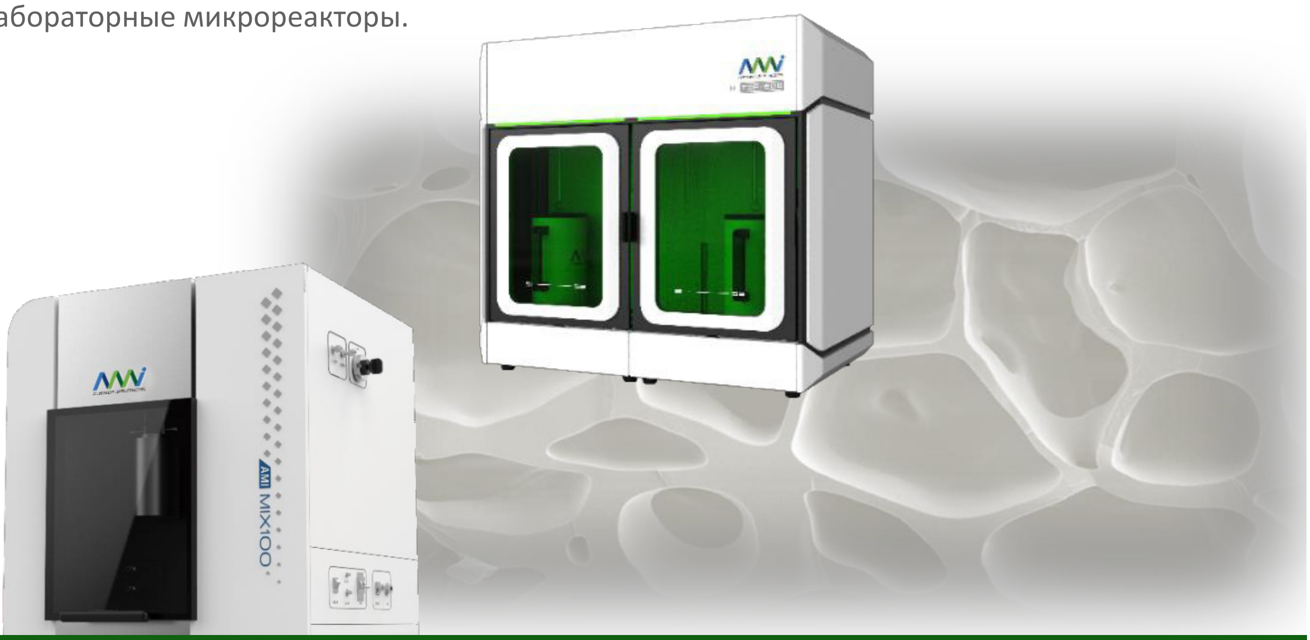
ИССЛЕДУЕМЫЕ МАТЕРИАЛЫ:

- ✓ Цеолиты
- ✓ Катализаторы
- ✓ Абсорбенты
- ✓ МОКС и др.

ХЕМОСОРБЦИОННОЕ ОБОРУДОВАНИЕ

исследование катализаторов: ТПО/ТПВ/ТПД реакции, импульсное титрование, in-situ определение ИК-спектров десорбции на кислотных/основных центрах.

- ✓ Анализаторы динамической хемосорбции;
- ✓ Лабораторные микрореакторы.



ПРОВЕДЕНИЕ ДЕМОНСТРАЦИОННЫХ АНАЛИЗОВ ВАШИХ ОБРАЗЦОВ В НАШЕЙ ЛАБОРАТОРИИ!

ПОСТАВКА ОБОРУДОВАНИЕ	ПОДБОР КОМПЛЕКТУЮЩИХ	МЕТОДИЧЕСКАЯ ПОДДЕРЖКА	ТЕХНИЧЕСКОЕ ОБСУЖИВАНИЕ

119071, Москва, Ленинский пр. 19, стр.1, +7 495 256-24-84, info@lab-test.ru, www.lab-test.ru

PLENARY LECTURES

Self-oscillating catalytic processes in metal-oxide and metal-carbon systems

A.I. Boronin

Boreskov Institute of Catalysis, Novosibirsk, Russia

boronin@catalysis.ru

Supported metal-oxide and metal-carbon catalysts are among the most important catalytic systems for various types of reactions, including oxidation reactions. For the theoretical analysis of catalytic mechanisms, the most popular and indispensable reaction is the oxidation reaction of CO on catalysts involving platinum metals supported on oxide and carbon supports. These catalysts allow detailed studying of the kinetics and dynamics of the CO oxidation reaction, that is of great interest from both a practical and theoretical point of view. In the experimental study of the kinetics of the CO oxidation reaction, various nonlinear phenomena are observed, such as hysteresis, self-oscillations, and chaotic dynamics of the reaction rate.

In this paper, experimental manifestations of self-oscillations observed in palladium catalysts at the micro- and nano-levels are considered. A detailed examination of the kinetics on the polycrystalline surface of palladium allowed us to establish the relationship between two nonlinear effects, namely: hysteresis and self-oscillations of the reaction rate of CO oxidation at elevated pressures of the reaction medium [1]. It was established that under heating the oxidation of metallic palladium to bulk palladium oxide occurred through formation of the palladium surface oxide. Under cooling the bulk oxide reduced directly to metallic species, and in this case some self-sustained oscillations of reaction rate were observed. The catalytic scheme including main various oxygen states of the palladium surface and bulk with transitions between them under reaction conditions in heating/cooling catalytic cycle was proposed.

Pd/Al_2O_3 supported catalysts, differed in the initial structural and chemical states of palladium, were examined for the possible existence of self-sustained oscillations in the reaction of CO oxidation under temperature-programmed and isothermal modes using plug flow reactor at ambient pressure and CO and O_2 concentration [2]. The supported samples after the action of reaction mixture were characterized using the HRTEM and XPS methods. During prolonged self-sustained oscillations under isothermal conditions with varying CO concentrations in the reaction mixture, particles with “core–shell” structures are formed, where the cores are PdO and the shells are a Pd^0 clusters ordered along a specific direction due to an epitaxy on PdO.

The oxidation of CO over Pd nanoparticles supported on carbon nanofibers (CNFs) and N-doped carbon nanofibers (NCNFs) has been studied. Investigation by STEM together with EEL spectroscopy revealed that Pd nanoparticles are located on the NCNFs surface patches that have a high concentration of N atoms. The N-doping of CNFs was shown to change the electric conductivity of N-CNFs and redox properties of Pd, which thus determines the self-oscillatory behavior of the catalysts during CO oxidation, the type of oscillations, and the conditions of their generation. Mechanisms that underlie the effect of N in N-CNFs on the electronic state of Pd as well as the occurrence of two types of oscillation mechanisms- the known redox mechanism and the mechanism related to Pd intercalation into graphene layers- are discussed [3].

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 (FWUR-2024-OO32).

References

1. Lashina E.A., Slavinskaya E.M., Chumakova N.A., Stadnichenko A.I., Salanov A.N., Chumakov G.A., Boronin A.I., Chem. Eng. Sci., 2020, 212, 115312–115327.
2. Slavinskaya E.M., Stonkusa O.A., Gulyaev R.V., Ivanova A.S., Zaikovskii V.I., Appl. Catal. A: General, 2011, 401, 83–97.
3. Stonkus O.A., Kibis L.S, Podyacheva O.Yu, Slavinskaya E.M, Zaikovskii V.I., Abdelwahab H.H., Hampel S., Leonhardt A., Ismagilov Z.R., Noskov A.S., Boronin A.I., ChemCatChem, 2014, 6, 2115–2128.

Gold catalysts for oxidation reactions

S.A.C. Carabineiro[1], E.N. Kolobova[2], E.G. Pakrieva[3], A.N. Pestryakov[2]

[1]LAQV-REQUIMTE, Department of Chemistry, NOVA School of Science and Technology, Universidade NOVA de Lisboa, Caparica, Portugal
[2]Research School of Chemistry & Applied Biomedical Sciences, Tomsk Polytechnic University, Tomsk, Russia
[3]Instituto de Nanociencia y Materiales de Aragon (INMA), CSIC-Universidad de Zaragoza, Campus Rio Ebro, Zaragoza, Spain

sonia.carabineiro@fct.unl.pt

For a long time, Au was only seen as a precious metal, used in coinage and ornaments. This was considered as inert and, therefore, not suitable for catalysis. However, once it was found that gold could be very active as nanoparticles, a new area of research began [1].

Nowadays, gold is already established as a very active catalyst for many reactions [2,3]. In particular, supported gold nanoparticles have demonstrated exceptional catalytic activity in a variety of industrially significant reactions, particularly in oxidation processes. Notably, the oxidation of alcohols [4-12], that are substrates with substantial industrial relevance, remains a challenging area.

In this talk, some examples on the use of gold as a catalyst for the oxidation of several alcohols will be given and the challenges remaining to be overcome will be addressed.

This work received support from FCT/MCTES, Fundação para a Ciência e Tecnologia and Ministério da Ciência, Tecnologia e Ensino Superior, Portugal) through projects DOIs: 10.54499/LA/P/0008/2020, 10.54499/UIDP/50006/2020, 10.54499/UIDB/50006/2020 and DOI 10.54499/CEECINST/00102/2018/CP1567/CT0026). This work was also supported by the Ministry of Education and Science of the Russian Federation Program No. 075-03-2024-118/1.

References

1. Bond G.C., Louis C., Thompson D.T., Catalysis by Gold, Imperial College Press: London, United Kingdom, 2006.
2. Carabineiro S.A.C., Thompson D., Catalytic Applications for Gold Nanotechnology. In Nanocatalysis, Heiz, U., Landman, U., Eds.; NanoScience and Technology; Springer: Berlin, Heidelberg, 2007, 377–489.
3. Carabineiro S.A.C., Thompson D., Gold Catalysis. In Gold: Science and Applications, Corti, C., Holliday, R., Eds.; CRC Press, Taylor & Francis Group: Boca Raton, London, New York, 2010, 89–122.
4. Pakrieva E., Kolobova E., Carabineiro S.A.C., Pestryakov A., Synthesis and Applications in Chemistry and Materials, 2024, 371–394.
5. Carabineiro S.A.C., Frontiers in Chemistry, 2019, 7, 702.
6. Martins L.M.D.R.S., Carabineiro S.A.C., Wang J., Rocha B.G.M., Maldonado-Hódar F.J., Pombeiro A.J.L.d.O., ChemCatChem, 2017, 9, 1211–1221.
7. Kolobova E., Mäki-Arvela P., Grigoreva A., Pakrieva E., Carabineiro S.A.C., Peltonen J., Kazantsev S., Bogdanchikova N., Pestryakov A., Murzin D.Y., Catalytic oxidative transformation of betulin to its valuable oxo-derivatives over gold supported catalysts: Effect of support nature. Catalysis Today 2021, 367, 95–110.
8. Grigoreva A., Kolobova E., Pakrieva E., Mäki-Arvela P., Carabineiro S.A.C., Gorbunova A., Bogdanchikova N., Murzin D.Y., Pestryakov A., Nanomaterials, 2021, 11, 469.
9. Kolobova E.N., Pakrieva E.G., Carabineiro S.A.C., Bogdanchikova N., Kharlanov A.N., Kazantsev S.O., Hemming J., Mäki-Arvela P., Pestryakov A.N., Murzin D.Y., Green Chemistry, 2019, 21, 3370–3382.
10. Pakrieva E., Kolobova E., Kotolevich Y., Pascual L., Carabineiro S.A.C., Kharlanov A.N., Pichugina D., Nikitina N., German D., Zepeda Partida T.A., et al., Nanomaterials, 2020, 10, 880.
11. Pakrieva E., Kolobova E., German D., Stucchi M., Villa A., Prati L., Carabineiro S.A.C., Bogdanchikova N., Cortés Corberán V., Pestryakov A., Processes, 2020, 8, 1016.
12. Liu L., Li H.Y., Tan Y., Chen X.K., Lin R.H., Yang W.S., Huang C.Q., Wang S.S., Wang X.P., et al., Catalysts 2020, 10.

Fundamentals for targeted design of catalysts efficiently producing propene via propane dehydrogenation

E.V. Kondratenko

Leibniz-Institut für Katalyse e.V., Rostock, Germany

evgenii.kondratenko@catalysis.de

The non-oxidative dehydrogenation of propane to propene is an ingenious technology that has been developed to bridge the gap between the supply and demand for this olefine [1,2]. Commercial catalysts based on chromium oxide or platinum suffer from the environmental incompatibility or high cost of the active components. Against this background, our research activities concentrate on the develop of sustainable alternatives. Our main objective is to establish fundamentals required for purposeful design of catalysts with industrially relevant performance [3-5]. In this talk, I will present and discuss recent results from my group to illustrate how such knowledge is generated and can be implemented in applied catalysis. The importance of controlling the structure of catalytically active sites/species for efficient catalyst functioning will be demonstrated. I will exemplify approaches for catalyst design combined with advanced mechanistic and kinetic studies as well as material characterization that enable establishing descriptors relevant to guide targeted catalyst development.

References

1. Otroshchenko T., Jiang G., Kondratenko V.A., Rodemerck U., Kondratenko E.V., Chem. Soc. Rev., 2021, 50, 473–527.
2. Chen S., Chang X., Sun G., Zhang T., Xu Y., Wang Y., Pei C., Gong J., Chem. Soc. Rev., 2021, 50 (5), 3315–3354.
3. Zhang Y., Zhao Y., Otroshchenko T., Lund H., Pohl M.-M., Rodemerck U., Linke D., Jiao H., Jiang G., Kondratenko E.V., Nature Commun., 2018, 9.
4. Zhao D., Tian X., Doronkin D.E., Han S., Kondratenko V.A., Grunwaldt J.-D., Perechodjuk A., Vuong T.H., Rabeah J., Eckelt R., Rodemerck U., Linke D., Jiang G., Jiao H., Kondratenko E.V., Nature, 2021, 599, 234–238.
5. Yang G-Q., Niu Y., Kondratenko V.A, Yi X., Liu C., Zhang B., Kondratenko E.V, Liu Z-W., Angew. Chem. Int. Ed., 2023, 62, e20231006.

Templated porous systems for catalytic oxidation and reduction processes

E. Lokteva, E.V. Golubina, I.Yu. Kaplin

Lomonosov Moscow State University, Moscow, Russia

LES@kge.msu.ru

It is known, that templated synthesis of metal oxides for the use as catalysts or their carriers provides many advantages: an increase in specific surface value, ensuring better dispersion of the supported active component; tuning of the pore sizes, creating regular or hierarchical porous system which reduces diffusion difficulties for reagents and products [1]. Less is known about the fact that using a template, you can also change the structure of the resulting material, which will further influence on the catalytic properties.

Not only artificially prepared materials, for example, surfactants or polymeric materials, can be used as templates. A separate group of templates includes biological materials - waste plant and animal biomass, viruses, microorganisms, etc. Their use allows to create nature-like textures, but in the other way it also allows to efficiently use waste for obtaining valuable products. Some biomass components provide a promoting effect on the resulting catalysts and carriers.

This lecture will describe examples of varying the texture and structure of several types of catalysts using template methods that provide good catalytic properties in the reactions of oxidative and reductive catalysis.

The main attention will be paid to the use of templated catalytic systems in the following catalytic processes: oxidation of CO in the absence (1) and (2) in the presence of excess hydrogen (PROX CO), (3) dehydrogenation of propane into propylene (PDH), (4) hydrodechlorination of the microecotoxicant diclofenac (HDC) in order to remove it from aqueous media.

For the reactions (1) and (2), oxide systems comprising CeO_2, ZrO_2, SnO_2, their mixed oxides, not-modified and modified by Cu or Mn oxides, were prepared using artificial (CTAB, Pluronic 123) and biotemplate (wood sawdust). The use of biotemplate is especially efficient to produce double CeZrOx systems. Cu- or Mn-modified catalysts prepared using artificial templates demonstrated improved efficiency in CO oxidation. Promoting action of ash impurities inherited by the catalysts from biomass template was demonstrated.

For the reaction (3), CrO_x-ZrO_2-SiO_2 catalysts were prepared using CTAB as template and rice husk in a dual role - as a template and a source of silicon oxide. The sample for which rice husk was first thermally decomposed to produce SiO_2, and then CrO_x and ZrO_2 were supported in the presence of CTAB, was more stable in PDH reaction, than one-pot sample and CTAB templated CrO_x-ZrO_2 system.

For the reaction (4), SiO_2 modified with ZrO_2 was prepared using CTAB template (mesoporous SiO_2ZrO_2), or Pluronic 123 (ordered mesoporous SiO_2ZrO_2 type SBA-15). ZrO_2 was added during structure formation or by post-synthetic treatment of SiO_2 in the form of SBA-15. Pd alone or together with FeO_x was supported on such carriers by wet impregnation. The use of ordered mesoporous support provides improved reducibility of Pd in very mild conditions (30°C, H_2) and better performance of the mildly reduced catalyst in comparison with the counterpart with not-ordered mesoporous texture. The synergistic interaction of FeO_x and ZrO_2 modifiers was observed. Such modified Pd catalyst demonstrated the highest activity in batch system and high stability in flow-type HDC of diclofenac in water at 30°C.

The reasons of the observed influence of a template nature on the catalytic properties will be discussed using the results of meticulous physical-chemical studies using XRD, XPS, TEM, SEM, EDA, Raman and IR-spectroscopy, TPR and other appropriate methods.

The authors thank Lomonosov Moscow State University Program of Development (access to XPS and TEM facilities). This work was supported by the Russian Science Foundation, Grant 22-23-00445, and RF State program 122040600057-3.

References

1. Kaplin I., Lokteva E., Golubina E., Lunin V., Molecules., 2020, 25(18), 4242.

Solid state NMR spectroscopy for studies of activation and conversion of light alkanes on metal-modified zeolites*

A.G. Stepanov

Boreskov institute of catalysis of the Siberian branch of Russian Academy of Sciences, Novosibirsk, Russia

stepanov@catalysis.ru

Large reserves of small alkanes of the C_1-C_4 composition in natural gas, gas condensate, and oils require their rational processing into more useful products for industry and everyday life. Processing of alkanes into useful products, such as aromatic hydrocarbons or oxygenates, is possible using metal-modified zeolite catalysts, i.e., zeolites (structural types are MFI, BEA, MOR, Y) with metals (Pt, Zn, Ga, In, Cu, Ag, Mo) being introduced into their pores in the form of cations or metal oxide particles. To understand the effect of the metal introduced into the zeolite on the direction of the reaction, it is necessary to know the mechanisms of alkane activation and conversion on the metal-modified zeolites. This opens ways to regulate the directions of alkane conversion and the development of catalysts capable of conducting the reactions along the path determined by the researcher obtaining the desired products.

Solid-state high-resolution magic-angle spinning NMR spectroscopy (HRMAS NMR) is a highly effective method to study the reaction mechanisms over heterogeneous catalysts that allows obtaining unique information on the mechanisms of activation and conversion of light hydrocarbons, which cannot be obtained by other methods.

The report defines general approaches to use HRMAS NMR to establish reaction mechanisms on the zeolite surfaces, presents the results of the NMR spectroscopic study of the mechanisms of activation and conversion of C_1-C_4 alkanes on MFI (ZSM-5) and BEA zeolites modified with Zn or In.

Methane activation on Zn/H-ZSM-5, Zn^{2+}/H-BEA, ZnO/H-BEA zeolites. The presence of a synergistic effect of zinc introduced into the zeolite and the Brønsted acid site (BAS) on the activation of C-H bonds in methane was established [1]. Significant acceleration of the H/D exchange of methane with the BAS was discovered upon modification of the zeolite with zinc [2]. Intermediates formed during the methane activation were identified [3]. Competitive activation pathways were established: H/D hydrogen exchange and formation of the zinc methyl intermediate (Zn-CH_3) [4]. Formation of the methoxy intermediate (O-CH_3) was detected [3], and the role of impurity molecular oxygen in its formation was established [5]. The directions of methane conversion in the presence of impurity molecular oxygen in the zeolite were revealed [5]. The mechanism of joint aromatization of methane and propane was established [6], and the role of oxygen in the possibility of its occurrence was clarified [7]. The role of different zinc species, Zn^{2+} cations and small ZnO clusters in the formation of the Zn-CH_3 intermediate was established [8].

Methane activation on InO^+/H-ZSM-5, InO^+/H-BEA zeolites. Analysis of the kinetics of H/D hydrogen exchange of methane and BAS of the zeolite showed the presence of two parallel processes during the activation: hydrogen exchange and the formation of a methyl-indium oxide intermediate that was due to the synergistic action of the BAS and InO^+ species in the methane molecule activation [9]. The methane conversion into oxygenates, including methanol and acetaldehyde, as well as the occurrence of a reaction of joint aromatization of methane and ethylene were detected [10].

Activation and conversion of propane on Zn/H-ZSM-5, Zn^{2+}/H-BEA, ZnO/H-BEA zeolites. Acceleration of the H/D exchange and its regioselectivity to the methyl group of the alkane were found upon the zinc introduction into the zeolite, which indicated the zinc effect on the activation of the C–H bonds of alkane on the BAS and the preferential activation of the methyl group of propane. Differences in the mechanisms of the H/D exchange on zeolites Zn^{2+}/H-BEA and ZnO/H-BEA were revealed [11]. The mechanism of propane conversion to aromatic hydrocarbons was established. Based on the analysis of the aromatization kinetics obtained by the ^{1}H HRMAS NMR in situ, a conclusion was made about the different efficiency of the Zn^{2+} cations and ZnO particles in the alkane aromatization [12].

Activation and conversion of propane on InO^+/H-ZSM-5, InO^+/H-BEA zeolites. Acceleration of the H/D exchange and its regioselectivity to the methyl group of alkanes in the presence of InO^+ cations in the zeolite were found. The kinetics of the H/D exchange was due to the contribution of two mechanisms that ensured the activation of the alkane and its involvement in the H/D exchange reaction [13]. The alkane conversion occurred through two directions: aromatization and oxidation to C_2–C_3 carboxylic acids [14].

References

1. Stepanov A.G., Arzumanov S.S., Gabrienko A.A., Parmon V.N., ChemPhysChem, 2008, 9, 2559.
2. Stepanov A.G., Arzumanov S.S., Gabrienko A.A., Toktarev A.V., Freude D., J. Catal., 2008, 253, 11.
3. Luzgin M.V., Rogov V.A., Arzumanov S.S., Parmon V.N., Angew. Chem., Int. Ed., 2008, 47, 4559.
4. Arzumanov S.S., Gabrienko A.A., Stepanov A.G., Catal. Sci. Technol., 2016, 6, 6381.
5. Gabrienko A.A., Arzumanov S.S., Luzgin M.V., Stepanov A.G., J. Phys. Chem. C, 2015, 119, 24910.
6. Luzgin M.V., Arzumanov S.S., Stepanov A.G., Parmon V.N., Catal. Today, 2009, 144, 265.
7. Stepanov A.G., Arzumanov S.S., Gabrienko A.A., Chem.: Methods, 2021, 1, 224–230.
8. Gabrienko A.A., Arzumanov S.S., Toktarev A.V., Danilova I.G., Freude D., Haase J., Stepanov A.G., ACS Catal., 2017, 7, 1818.
9. Arzumanov S.S., Freude D., Haase J., Stepanov A.G., J. Phys. Chem. C, 2014, 118, 14427.
10. Gabrienko A.A., Arzumanov S.S., Toktarev A.V., Stepanov A.G., J. Phys. Chem. C, 2014, 118, 8034.
11. Arzumanov S.S., Gabrienko A.A., Toktarev A.V., Stepanov A.G., J. Catal., 2019, 378, 341−352.
12. Arzumanov S.S., Gabrienko A.A., Lashchinskay Z.N., Stepanov A.G., J. Phys. Chem. C, 2019, 123, 30473.
13. Arzumanov S.S., Gabrienko A.A., Toktarev A.V., Stepanov A.G., J. Phys. Chem. C, 2022, 126, 19766.
14. Gabrienko A.A., Arzumanov S.S., Toktarev A.V., Prosvirin I.P., Freude D., Haase J., Stepanov A.G., J. Phys. Chem. C, 2022, 126, 16204.

---

*Original abstract was written in Russian language. The abstract was translated by PhD M.A. Salaev.

Gold catalysts for hydrogen production via water-gas shift reaction: insight into role of support

T. Tabakova

Institute of Catalysis, Bulgarian Academy of Sciences, Sofia, Bulgaria

tabakova@ic.bas.bg

Hydrogen is gaining global interest as an alternative energy source to address environmental issues. The growing demand for hydrogen and advancement in fuel cell technology has led to renewed interest in the water-gas shift (WGS) reaction. Efficiently upgrading hydrogen purity for fuel cell applications imposes new goals and challenges in designing WGS catalysts. Among variety of compositions developed for high- and low-temperature shift reaction, supported gold catalysts attract significant attention during the last three decades. Compared to commercial WGS catalysts, the main advantage is the combination of high activity at low temperature and favorable features enabling use in small scale applications such as residential fuel cells or on-board hydrogen generators. Various strategies and approaches have been developed to design efficient gold-based catalysts. Emphasis was placed on exploring appropriate carriers, recognizing the crucial role of support in determining catalytic activity. The support may participate in the reaction or control catalytic behavior by affecting gold-support interface interaction, shape and gold particle size, and stabilization of gold's structural/electronic properties.

Among various metal oxides, ceria-based gold systems received special interest. Numerous studies of Au/CeO_2 catalysts have addressed how various factors, including preparation method, gold loading and gold particle size, structure and oxidation state, and reactivity of surface species correlate with catalytic performance in the WGS reaction. The modification of ceria was considered as an important approach for improvement of WGS activity of gold/ceria catalysts. Different additives (Sm, La, Zn, Fe, Mn, Sn, Y) were incorporated in ceria lattice in order to increase the amount of oxygen vacancies owing to their crucial role in water dissociation. The role of Fe as dopant of Au/CeO_2 catalysts was investigated in depth. The influence of mixed Ce-Fe oxides preparation approach and composition were studied. Significantly higher activity of gold catalysts on mechanochemically prepared supports in comparison with those on impregnated Fe-Ce oxides was explained with the availability of higher amount highly dispersed Au nanoparticles and the presence of separate defective magnetite phase. Significant effect on the WGS performance of Au/ceria catalysts was achieved by Y-doped ceria. The influence of synthesis route and Y_2O_3 loading was examined.

Preparation of appropriate and economically profitable carriers with complex composition by various synthesis procedures emerged as a successful strategy for WGS performance improvement. Commercial γ-alumina was modified with well dispersed surface fraction of Ce–Fe, Ce-Zn or Cu-Mn mixed oxides and used as a support of gold-based catalysts. This synthesis concept allows maximizing the activity per mass of gold due to its high dispersion on the support surface, thus achieving greater interfacial area between gold nanoparticles and supported on alumina mixed oxides, as well as enhanced oxygen mobility. Novel catalytic systems with enhanced efficiency for the WGS reaction were thoroughly investigated, harnessing the advantageous properties of hydrotalcite materials (CuO-ZnO-Al_2O_3 or NiO-Al_2O_3) and supported gold nanoparticles.

Upon analyzing the correlation between WGS activity and carrier characteristics, it becomes evident that employing the right chemical composition and synthesis method enables the development of gold catalysts with highly promising practical applications.

Revealing the scale-up problems in the production of Pd-containing catalysts

A.A. Vedyagin

Closed Joint Stock Company "Nizhegorodskiye Sorbenty", Nizhniy Novgorod, Russia

vedyagin@nsorbent.ru

Nowadays, palladium catalysts are widely applied in numerous industrial processes, such as hydrogenation, hydroisomerization, dehydrogenation, total and preferential oxidation, etc. As announced by the Verified Market Reports, the Palladium Catalyst Market size was valued at USD 16.5 Billion in 2023.

Among palladium-containing oxidation catalysts, diesel oxidation catalysts, and three-way catalysts, which are aimed at neutralizing vehicle exhaust gases, are of special interest. There are special requirements for such catalysts. For example, three-way catalysts used in the case of gasoline internal combustion engines should provide simultaneous oxidation of unburned hydrocarbons and CO, as well as the reduction of nitrogen oxides. At the same time, they must be resistant to high temperatures (1000 °C and above) without significant loss of activity. Unfortunately, the Pd-only catalysts do not meet such requirements for thermal stability. At temperatures above 800 °C, palladium particles migrate along the surface of the support and agglomerate, which leads to deactivation of the catalyst [1]. As a promising approach to the thermal stabilization of three-way catalysts, the target formation of bimetallic Pd-Rh particles of the alloy type, as well as a decrease in the loading of active metals to a level corresponding to the concentration of electron-donor sites on the support surface can be singled out [2]. In this case, the catalysts exhibit appropriate stability at elevated temperatures due to strong metal-metal and metal-support interactions. The attractiveness of this approach lies in the possibility, if necessary, of introducing a third metal into the alloy [3].

It should be noted that the fundamental studies described above were carried out on a model γ-Al_2O_3 support, which is practically not used in pure form to produce commercial catalysts. This is primarily due to its low thermal stability. This problem is exacerbated by the presence of rhodium ions, capable of initiating phase transitions followed by the α-phase formation at ~ 900 °C. To solve the problem of thermal stability, manufacturers use special brands of aluminum oxide doped with lanthanum or zirconium oxides, or in mixtures with more complex oxide compositions (for example, $ZrCeYLaO_2$). In the case of real supports, the effects of stabilization of active metals in the form of bimetallic particles can persist or weaken [4,5].

Another important problem in scaling up the production technology of the Pd-containing catalyst is the necessity of additional processing steps or the addition of odd components. For example, in the case of La-promoted alumina, prolonged interaction of the support with the impregnating solution in the mode of intensive mixing leads to the washing out of lanthanum into the solution, thus resulting in the reduced thermal stability of the support [6]. Another example is the addition of barium nitrate to improve the rheological properties of the slurry used for deposition on the cordierite monoliths. Recently, it has been shown that barium nitrate can have both positive and negative effects on the activity and stability of the catalysts [7].

References

1. Vedyagin A.A., Volodin A.M., Stoyanovskii V.O., Mishakov I.V., Medvedev D.A., Noskov A.S., Appl. Catal. B: Environ., 2011, 103, 397–403.
2. Vedyagin A.A., Volodin A.M., Kenzhin R.M., Stoyanovskii V.O., Shubin Y.V., Plyusnin P.E., Mishakov I.V., Catal. Today, 2017, 293–294, 73–81.
3. Vedyagin A.A., Shubin Y.V., Kenzhin R.M., Plyusnin P.E., Stoyanovskii V.O., Processes, 2020, 8, 928.
4. Vedyagin A.A., Kenzhin R.M., Tashlanov M.Y., Stoyanovskii V.O., Plyusnin P.E., Shubin Y.V., Mishakov I.V., Kalinkin A.V., Smirnov M.Y., Bukhtiyarov V.I., Emiss. Control Sci. Technol., 2019, 5, 363-377.
5. Vedyagin A.A., Alikin E.A., Kenzhin R.M., Tashlanov M.Y., Stoyanovskii V.O., Plyusnin P.E., Shubin Y.V., Mishakov I.V., Reac. Kinet. Mech. Catal., 2020, 129, 117–133.
6. Stoyanovskii V.O., Vedyagin A.A., Ceram. Int., 2022, 48, 17449–17459.
7. Alikin E.A., Baksheev E.O., Veselov G.B., Kenzhin R.M., Stoyanovskii V.O., Plyusnin P.E., Shubin Y.V., Vedyagin A.A., J. Environ. Chem. Eng., 2024, 12, 112945.

KEYNOTE LECTURES

The role of graphene-like carbon layer and metal core in catalytic activity of metal-carbon nanocomposites

E.V. Golubina, E.S. Lokteva

Lomonosov Moscow State University, Department of Chemistry, Moscow, Russia

golubina@kge.msu.ru

The development of a convenient and affordable method of preparation of catalysts based on nanosized metal particles is essential for the design of highly active metal catalysts. Interaction between catalysts components is one of the important factors controlling the catalytic activity of supported metal particles. Since the reactions involving H_2 activation are very important in industrial catalysis, this step is important for considering in catalysts design.

Several types of metal-carbon composites are considered in this work. **M-C** (M = Ni, Pd) samples were prepared by) pyrolysis of sawdust impregnated with corresponding metal salts [1]. **M@C** (M = Ni, Pd, Fe) samples were prepared by evaporation of overheated liquid metal drops in the flow of Ar containing an admixture of butane as described in [2] by group of Prof. A.Ye.Yermakov (Institute of Metal Physics, Ural Branch, Russian Academy of Sciences, Yekaterinburg, Russia). All samples were characterized by N_2 adsorption/desorption, XPS, SEM, TEM, Raman spectroscopy, TPR-H_2. Catalytic activity was tested in chlorobenzene hydrodechlorination and phenylacetylene hydrogenation in flow-type fixed-bed reactor.

M-C composites consist of a carbon matrix and metal nanoparticles coated with a thin layer of carbon shell. The proposed one-step method makes it possible to obtain metal nanoparticles without additional reduction steps. XPS study showed formation of metallic palladium already at the first stages of pyrolysis. The particle size can be varied from 2 to 9 nm by the pre-treatment of wood sawdust under hydrothermal or thermo-steam conditions. M@C catalysts are metal nanoparticles (4-5 nm) coated with a graphene-like shell. According to TEM and Raman M@C samples, unlike M-C, do not contain a matrix of activated carbon. The formation of a carbon shell is determined by the metal and the method of preparation. Thus, the Pd@C shell is formed poorly, and the particles become larger, while during of sawdust pyrolysis carbon-coated stable Pd nanoparticles are formed.

Both M-C and M@C catalysts showed excellent activity in hydrodechlorination and hydrogenation reactions. All Pd-C provide chlorobenzene conversion up to 90%. Natural ash impurities in sawdust act as promoters, increasing activity in the low-temperature region Both Ni@C and Fe@C provide high conversion of phenylacetylene (close to 100%) at the temperatures above 150 and 300 °C, respectively. Excellent styrene selectivity (86% at 99% conversion at 300 °C) was obtained in the presence of Fe@C.

Carbon shell contributes to the stabilization of nanosized metal particles and does not hinder catalytic activity. Ni@C and Fe@C samples in which non-carbon-coated metal particles have been completely removed remains active in the hydrogenation reaction. Thus, the reaction occurs on the surface of the carbon layer in contact with the metal core. Additional experiments involving H_2:D_2 =1 gas mixture instead of pure H_2 give evidence of the ability of graphene-like carbon shell to H_2 activation by dissociative adsorption. It became possible due to the presence of structure defects in graphene layer and the presence of transition metal in subsurface layer. Since molecular hydrogen dissociation is the key step of hydrogenation reactions, these facts provide high efficiency of core-shell metal-carbon nanocomposites.

This work was supported by the State Assignments of MSU (AAAA-A21-121011990019-4). The authors acknowledge support from the Lomonosov Moscow State University Program of Development for providing access to the TEM and XPS facilities.

References

1. Lokteva E.S., Klokov S.V., Golubina E.V., Maslakov K.I., Trenikhin M.V., Ivakin Y.D., Likholobov V.A., Russian Chemical Bulletin, 2016, 65, 2618–2627.
2. Galakhov V.R., Shkvarin A.S., Semenova A.S., Uimin M.A., Mysik A.A., Shchegoleva N.N., et al., J Phys Chem C, 2010, 114 (51), 22413–6.

Nanostructured photocatalysts based on g-C_3N_4 for visible light-induced CO_2 reduction

A. Kurenkova[1], D. Vasilchenko[1,2], A. Saraev[1], E. Kozlova[1]

[1]Boreskov Institute of Catalysis, Novosibirsk, Russia
[2]Nikolaev Institute of Inorganic Chemistry, Novosibirsk, Russia

kozlova@catalysis.ru

The global trend towards decarbonization of economies and energy systems requires the development of new energy sources. In addition, the annually increasing emissions of greenhouse gases, especially CO_2, from the combustion of fossil fuels lead to the removal of carbon from the energy cycle. Catalytic conversion of CO_2 into synthetic fuels is a promising method to address these problems; for example, the process of synthesizing methane from CO_2 is already used in industry [1]. Nickel-based catalysts are widely used for CO_2 methanation because of the low cost of the metal. However, such catalysts do not have high activity at low temperatures and are destroyed at high temperatures. Therefore, the development of new approaches to the synthesis of catalysts for the efficient conversion of CO_2 to methane is an actual direction. On the one hand, by modifying the active component of the catalyst, for example, by adding other metals and "tuning" the carrier, the stability and activity of the catalyst can be improved. Another approach to improving the activity and stability of the catalyst is to use additional light energy stimulation to lower the CO_2 conversion temperature. Photocatalytic reduction of CO_2 under light irradiation can occur at room temperature and atmospheric pressure. Using sunlight as an energy source, the process of synthesizing methane from CO_2 simultaneously allows carbon to be returned to the energy cycle and stores sunlight energy as chemical bonding energy [2].

The main factor hindering the practical implementation of photocatalytic CO_2 reduction processes is the lack of efficient and stable heterogeneous photocatalysts operating under the influence of visible light. Recently, the attention of the researchers has been attracted by the semiconductor polymer material graphite-like carbon nitride g-C_3N_4. This material has the properties of a semiconductor with the band gap energy equal to 2.7 eV, and the positions of valence band and conduction band suitable for the reduction of CO_2 [3]. This lecture describes the development of efficient photocatalysts based on g-C_3N_4 for photostimulated conversion of CO_2 to methane, including ternary heterostructures based on transition metals, their oxides (Fe_2O_3, NiO, Co_3O_4), g-C_3N_4 and rGO. The MOx/M/g-C_3N_4 (M = Fe, Ni, Co) composites realize the charge separation mechanism according to the classical Z-scheme, while MOx/g-C_3N_4 and rGO/g-C_3N_4 composites realize the charge separation mechanism according to the direct Z-scheme. Consideration of both direct and classical Z-scheme will allow to establish the influence of metal and its nature on the activity and selectivity of the catalyst in the target process. The relationship between the characteristics of materials based on graphite-like carbon nitride and their activity and selectivity for organic products in the reduction of carbon dioxide will be discussed. In addition, the study of the mechanism of the CO_2 reduction reaction using DRIFTS and XAS methods in *in situ/operando* mode will be considered.

The results obtained will provide a scientific basis for the development of a highly efficient catalyst for photo-stimulated CO_2 conversion with simultaneous solar energy storage.

This work was supported by the Russian Science Foundation, Grant 24-43-03010.

References

1. Alekseev R.F., Saraev A.A., Kurenkova A.Y., Kozlova E.A., Russ. Chem. Rev., 2024, 93, RCR5124:1–21.
2. Kozlova E.A., Lyulyukin M.N., Kozlov D.V., Parmon V.N., Russ. Chem. Rev., 2021, 90, 1520–1543.
3. Zhurenok A.V., Vasilchenko D.B., Kozlova E.A. Int. J. Mol. Sci., 2023, 24, 346.

New catalyst for efficient hydrogen evolution reaction based on Ag-doped Cu nanosheet arrays

L.J. Kong[1], S.A. Kulinich[2], X.W. Du[1]

[1]Tianjin University, Tianjin, PR China
[2]Tokai University, Hiratsuka, Japan

skulinich@tokai-u.jp

Development of novel catalysts for the hydrogen evolution reaction (HER), especially those with low cost and high activity, is very crucial for energy conversion. To date, numerous efforts have been made to find low-cost substitutes to the currently used catalysts based on noble metals [1]. In the present work, we adopted the method of sherardizing [2,3], which is typically used to protect steel against corrosion by immersing in molten zinc, to obtain self-supported nanosheet arrays of Cu doped with Ag (the two elements being immiscible naturally). Both experimental and theoretical results showed that the larger atomic radius of Ag introduces tensile stress into the newly formed material, adjusting the electronic structure of Cu components. The as-generated tensile strain results in a lower electron density at s-orbitals of Cu atoms and higher affinity to receiving electron density from adsorbates, which leads to their stronger adsorption. As such, an electrode based on the as-prepared Cu-Ag nanosheet arrays achieved a low overpotential of 103 mV at 10 mA cm^{-2} in 1 M KOH, which is 604 mV lower than that of pure copper foil. In addition, the electrode maintained 90 % of its performance after a 50-h-long stability test.

References

1. Greiner M.T., Jones T.E., Beeg S., Zwiener L., Scherzer M., Girgsdies F., Piccinin S., Armbruster M., Knop-Gericke A., Schlogl R., Nat. Chem., 2018, 10, 1008–1015.
2. Culcasi J.D., Seré P.R., Elsner C.I., Di Sarli A.R., Surf. Coat. Technol., 1999, 122, 21–23.
3. Long J.B., Li X.B., Zhong Y.C., Peng D., Trans. Indian Inst. Met., 2019, 72, 2443–2448.

The hard way from pure science to manufacturing scaling up

M.A. Lazarev[1,2]

[1]*Orgkhim Biochemical Holding, CJSK, Nizhny Novgorod, Russia*
[2]*Research Institute of chemistry of Nizhny Novgorod State University, Nizhny Novgorod, Russia*

m.lazarev@orgkhim.com

We live in a very interesting time. Often times circumstances change quicker than we manage to get used to the last adopted action model. The design-to-manufacturing sequence thoroughly elaborated and mastered over the years of state-purchasing framework has proven on many occasions incapable to deliver the quick response dictated by the modern-day business. Frequently the demand for a product, especially for import replacement purposes, is high now and today, but the system is only capable to make it available two or three years from now. Alternative ways to take a product from idea to manufacturing, for examples through minor entrepreneurship or startups, are to the contrary rather quick, but often poorly structured and not as effective. Thus, developing an efficient concept-to-manufacturing sequence, particularly end customers oriented, remains a relevant challenge for today’s Russian science and business.

Since its foundation in 2001 Orgkhim Biochemical Holding has been focusing on innovation and on integrating new products and technological processes into its existing production. The company opened up an in-house Research center in 2003. Since most of industry-specific RnD facilities had closed in the 90-ies because of short-funding thus signaling a virtual collapse of the national industrial-scientific program, the company had to look for alternative non-classical partnerships to do its research and development, test and design, and process related works, by partnering with scholars, with private engineering companies, including foreign ones, or chose to restore the somewhat eroded competencies with the help of one’s RnD facility. Numerous national oil-and-gas companies, to the contrary, opted to adopt licensed international processes in their manufacturing facilities thus forcing the gap between the national science and industry grow yet wider.

With time Orgkhim managed to build reliable scientific partnerships. Thus, Orgkhim Biochemical Holding has been successfully and fruitfully cooperating with the Lobachevsky State University of Nizhny Novgorod for a long time now (over 15 years). This specific partnership in particular resulted in two projects already implemented under the Russian Federation Government Order # 218: a cross-discipline project “High tech Production Development Based on Innovative Deep Processing of the Wood Industry Liquid Wastes” in 2013-2015 (subject code 02G25.31.0073) and “High tech Production Development of Non-Carcinogenic Oils-Plasticizers for Tires, Rubbers and Plastics Based on Innovative Petroleum Industry Wastes Processing” in 2016-2018 (subject code 02G.25.31.0165). Thanks to implementation of the aforementioned project, Orgkhim was successful in launching a non-carcinogenic extender oil production in Malaysia, in 2019 within a very tight time frame.

Orgkhim’s product development approach is an ever-evolving live system, therefore the information presented herein is relevant for the time being. This paper is designed to be of importance for young scientists, making their first steps in science, but keen to keep them thought-through and with an eye on transitioning their ideas to manufacturing in future. There are four parts in this paper. The main focus is on the positive implementation experience and on the management methods and tools which were instrumental in achieving success.

Ni and Ni-Ru catalysts over $LaMnO_3$ for methane decomposition to H_2 and catalyst regeneration by CO_2

E. La Greca[1,2], V. La Parola[1], G. Pantaleo[1], L. Consentino[1,2], M. Gruttadauria[2], R. Fiorenza[3], S. Scirè[3], L.F. Liotta[1]

[1]*Institute for the Study of Nanostructured Materials (ISMN), (Italian) National Research Council (CNR), Palermo, Italy*
[2]*STEBICEF Department Ed. 17, University of Palermo, Palermo, Italy*
[3]*Department of Chemical Science, University of Catania, Catania, Italy*

leonardafrancesca.liotta@cnr.it

Hydrogen is a good energy carrier due to its efficiency and lack of CO_2 evolution. Currently H_2 is mainly produced via steam reforming of natural gas requiring costly and complicated separations. For this reason, simple and efficient methods of H_2 generation are of significant interest. Catalytic methane decomposition is a promising method for H_2 production especially when coupled with the use of CO_2 to regenerate the catalyst from coke deposition.

The preparation methods for these catalysts are critical in designing their structure, thereby influencing their performance in methane decomposition applications. This study examines the performance of Ni supported on $LaMnO_3$ synthesized through precipitation assisted by microwave irradiation and sol-gel citrate methods. Moreover, being the addition of Ru known to stabilize Ni against sintering and to minimize coke deposition, bimetallic Ni-Ru catalysts were also prepared. The catalytic tests were performed carrying out multiple redox cycles, consisting in methane partial oxidation and methane decomposition to H_2 occurring over metallic Ni, formed in situ, and successive regeneration of the catalyst under CO_2, aiming to reoxidize the sample and remove the deposited carbon coke. The experiments were realized alternating the gas composition every 10 minutes between 15 vol% CH_4 in N_2 (reduction) and 15 vol% CO_2 in N_2 (oxidation) at isothermal conditions. The reaction temperature for each sample was determined from temperature programmed reduction tests with methane, selecting the temperature of maximum reduction for each sample.

By conducting comprehensive structural and morphological analyses and catalytic tests, this study highlights the impact of synthesis techniques on the performance of these samples in hydrogen production and provides valuable insights crucial for developing new efficient catalysts.

Project "Capitale Naturale e Risorse per il Futuro dell'Italia" (FOE 2020, Programma di Ricerca e Innovazione dal titolo "NEST - Network 4 Energy Sustainable Transition", (Partenariato Esteso – PE0000021, CUP B53C22004060006) and (PNRR) - missione 2 "rivoluzione verde e transizione ecologica" – componente 2 "energia rinnovabile, idrogeno, rete e mobilità sostenibile" – investimento 3.5 "ricerca e sviluppo sull'idrogeno" – AdP ENEA-CNR (CUP B93C22000630006) are acknowledged for financial support.

References

1. Grabchenko M.V., Dorofeeva N.V., Svetlichnyi V.A., Larichev Y.V., La Parola V., Liotta L.F., Kulinich S.A., Vodyankina O.V., Nanomaterials, 2023, 13 (19), 2641.
2. Salaev M.A., Liotta L.F., Vodyankina O.V., International Journal of Hydrogen Energy, 2022, 47 (7), 4489–4535.
3. Horváth A., Németh M., Beck A., Sáfrán G., La Parola V., Liotta L.F., Žerjav G., Roškarič M., Pintar A., Applied Catalysis A: General, 2024, 669, 119495.

Oxoanionic complexes of platinum group metals: solution speciation, isolation and utilization for catalysts preparation

D. Vasilchenko

Nikolaev Institute of Inorganic Chemistry, Novosibirsk, Russia

vasilchenko@niic.nsc.ru

The platinum-rhodium-palladium triad has an honorable role and an entire era in industrial catalysis due to their non-alternative use in the production of catalysts for neutralizing exhaust gases of internal combustion engines [1,2]. The role of these metals is no less significant for other areas of heterogeneous catalysis, as well as in the field of homogeneous catalysis. In the preparation of heterogeneous catalysts, starting metal compounds (precursor compounds) play an important role, from which they are applied to the carrier material. The overwhelming number of academic works and many industrial methods of preparing catalysts use chlorocomplexes or chlorides of these metals as precursor. On the other hand, chloride ions are often a catalytic poison and have a corrosive effect on the carrier material [3,4]. Other compounds of platinum group metals (PGM) can not only perform the function of a precursor, but also significantly surpass chlorocomplexes in terms of the activity of the formed catalysts, their stability and ease of preparation. The optimal precursor compound can be selected for each specific process and depending on the carrier material.

Nitrate systems - nitric acid solutions of rhodium and platinum (solutions of rhodium and platinum nitrate), palladium nitrate - are the most widely used of such alternatives to halides of precursors on an industrial scale. Despite the great practical relevance, the systematic study of nitrate complexes formed and existing in nitric acid solutions of the platinum-rhodium-palladium triad has not been given significant attention by researchers. The same can be said in general about solutions of these metals in mineral oxoacids and complexes of PGM with oxoanions in general.

This work presents the results of a comprehensive study on the oxyanionic complexes of MPG, which are derivatives of aqua-and aqua-hydroxo complexes obtained by replacing water molecules with corresponding anions - residues of inorganic acids such as nitric, sulfuric and carbonic. The work begins with a detailed examination of the methods used to prepare the corresponding solutions, and provides insight into the speciation of PGM in these solutions. As a result of the PGM speciation analysis, methods were developed to isolate individual oxyanion complexes into solid crystalline phases. The potential of PGM's oxyanions as effective precursors is illustrated through examples of the preparation of catalytic materials with promising activity in processes such as photocatalytic hydrogen production, CO oxidation and selective decomposition of hydrazine.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation, project No. 121031700315-2.

References

1. Wallington T. J., Anderson J. E., Dolan R. H., Winkler S. L., Atmosphere., 2022, 13, 650.
2. Tang H., Peng Z., Tian R., Ye L., Zhang J., Rao M., Li G., J. Environ. Chem. Eng., 2023, 11, 110237.
3. Zhu X., Cheng B., Yu J., Ho W., Appl. Surf. Sci., 2016, 364, 808–814.
4. Sun C., Wen, R., Qin Y., Wang L., Wang Y., Dou M., Wang F., ACS Appl. Energy Mater., 2023, 6, 5700–5709.

Structure – RedOx – DeNO$_x$ activity relationships for Cu-ZSM-5 catalysts

S.A. Yashnik

Boreskov Institute of Catalysis, Novosibirsk, Russia

yashnik@catalysis.ru

Diesel engines remain competitive in the modern transport market due to high values of thermal efficiency, productivity and efficiency of their operation, low emission of carbon dioxide with exhaust gases. Despite these advantages, since 2015, diesel vehicles have been severely criticized for releasing high amounts of nitrogen oxides and soot into the environment. The current standards regulate NOx emissions for light trucks of no more than 80 mg/km [1], and for heavy trucks of no more than 0.4 g/kWh [2]. To neutralize NOx, catalytic systems are built into the exhaust tract of trucks, selectively reducing NO_x with ammonia (SCR NO_x-NH_3) to molecular nitrogen.

In this work, characteristics of Cu-substituted ZSM-5 zeolites such as copper content, copper state, reducibility, ammonia sorption capacity, and SCR NO_x-NH_3 behavior will be discussed in order to reveal the structure – RedOx – activity relationships. To identify the synthesis and structure-activity relationship correlations, the ammonia solution and Cu-ZSM-5 samples were characterized by EPR, UV-visible spectroscopy, temperature-programmed reduction by hydrogen (H_2-TPR) and temperature-programmed desorption of ammonia (NH_3-TPD). Effect of water vapor (3-5 vol.%) and NO_2 (100 – 200 ppm) in the feeds on the SCR NO_x-NH_3 behavior of the catalyst will also be considered.

Cu-substituted ZSM-5 catalyst is synthesized mainly by ion exchange with aqueous solutions of copper salts, while copper content regulation is achieved by varying the concentration of copper in the solution or by multiplicity of ion exchange procedures [3, 4]. The use of aqueous-ammonia solutions of copper salts makes it possible to increase the total copper loading in Cu-ZSM-5 in one ion exchange procedure [3, 4] and form a larger number of structures of Cu^{2+} ions with extra-lattice oxygen (Cu^{2+}-ELO) [3, 5, 6]. Both of these factors contribute to an improvement in NO_x conversion; however, a high concentration of Cu^{2+}-ELO favors non-selective oxidation of NH_3 [7, 8].

For all the studied copper salts [3, 5, 6, 9], the sorption capacity of H-ZSM-5 for Cu^{2+} ions was the highest in copper-ammonia solutions with NH_4OH/Cu^{2+} =6, it decreased markedly with an increase in NH_4OH/Cu^{2+} to 30. The parameters of Langmuir, Freundlich, Dubinin-Radushkevich, and Temkin isotherms revealed the favorability of the chosen conditions (0.015–0.15 M of copper salt and NH_4OH/Cu^{2+} =6–30) and the chemical nature of $[Cu(NH_3)_4]^{2+}$ ions sorption by zeolite. The reducibility of Cu-ZSM-5 improved with an increase in the copper loading and with a decrease in NH_4OH/Cu^{2+}.

The calcined Cu-ZSM-5 samples produced at NH_4OH/Cu^{2+} =30 contained two types of the isolated Cu^{2+} ions. At NH_4OH/Cu^{2+} =6–10, the samples additionally comprised the Cu^{2+}–ELO structures. Cu^{2+}–ELO structures possessed a greater reducibility than both types of isolated Cu^{2+} ions.

The structure-activity relationship correlations [7, 8] revealed that the mono- and polynuclear structures of Cu^{2+} ions with ELO formed at NH_4OH/Cu^{2+} =6–10 and high Cu-loadings in the solutions of copper salts tend to be more active in NO-NH_3 SCR than the isolated Cu^{2+} ions.

This work was supported by the Ministry of Science and Higher Education of Russian Federation within the government order for BIC, Grant FWUR-2024-0033.

References

1. Regulation (EC) No 715/2007.
2. Regulation (EC) No 595/2009.
3. Yashnik S.A., Ismagilov Z.R., Anufrienko V.F., Catal. Today, 2005, 110, 310–322.
4. Tsikoza L.T., Matus E.V., Ismagilov Z.R., Sazonov V.A., Kuznetsov V.V., Kin. & Catal., 2005, 46 (4), 613–617.
5. Yashnik S.A., Ismagilov Z.R., Appl. Catal. B: Environ., 2015, 170-171, 241–254.
6. Yashnik S.A., Ismagilov Z.R., Kin. & Catal., 2016, 57, 776–796.
7. Yashnik S.A., Ismagilov Z.R., Appl. Catal. A: Gen., 2021, 615, 118054.
8. Yashnik S.A., Ismagilov Z.R., Top. Catal. 2019, 62, 179–191.
9. Yashnik S.A., Surovtsova T.A., Salnikov A.V., Microporous Mesoporous Materials, 2024, 367, 112966.

SECTION 1

CATALYST PREPARATION

In-situ SAXS study of Pt-contained solutions as catalytic precursors

Yu.V. Larichev

Boreskov Institute of Catalysis, Novosibirsk, Russia

ylarichev@gmail.com

Supported Pt catalysts are widely used in the modern chemical industry. Despite the existence of a large number of different methods for the preparation of Pt catalysts, there are continued developments of new methods for the preparation and/or modification of existing methods to obtain optimal characteristics of the supported platinum nanoparticles. One of such prospective methods is the hydrolysis of platinum nitrate in a water medium (as Cl - free synthesis), followed by the formation of polynuclear platinum hydroxocomplexes. Further these complexes are transformed into supported Pt nanoparticles upon contact with a support and heat treatment. The structure of mononuclear Pt nitrate complexes in concentrated acid medium has been studied by EXAFS and NMR previously [1, 2]. Nevertheless the understanding of processes of hydrolysis with the formation of nanosized Pt polyhydroxocomplexes and stabilization of their structures in solutions is still unclear at present. At present time there is not enough detailed information about mechanisms of formation/aggregation of polynuclear platinum hydroxocomplexes in solutions, their shapes and sizes. Whereas this information can be very relevant for understanding the processes of formation of supported nanoparticles during the impregnation of the porous supports with a solution containing the initial Pt polyhydroxocomplexes as a precursor of Pt nanoparticles. Therefore, in our work, we used the SAXS method to study the formation of platinum polynuclear hydroxocomplexes in water solutions in situ. Depending on the different stabilizers in Pt solutions is shown a different rate of particle aggregation processes. The shape and size of particles of platinum hydroxocomplexes in solution also have been established. Based on the obtained data on the growth kinetics, assumptions were made about the mechanism of Pt-contained particle aggregation in water solutions.

The work was financially supported by the Ministry of Science and Higher Education of the Russian Federation under the state assignment of the Boreskov Institute of Catalysis, project FWUR-2024-0032.

References

1. Dou D., Liu D.-J., Williamson W.B., Kharas K.C., Robota H.J., Appl. Catal. B, 2001, 30, 11–24.
2. Vasilchenko D., Tkachev S., Baidina I., Korenev S., Inorg. Chem., 2013, 52, 10532–10541.

Synthesis of finely dispersed carbon-coated calcium aluminate

Y.Y. Gerus, A.F. Bedilo, E.V. Ilyina, E.I. Shuvarakova

Boreskov Institute of Catalysis, Novosibirsk, Russia

ygerus@catalysis.ru

Of particular interest is the calcium aluminate $12CaO{\bullet}7Al_2O_3$, known as mayenite. This material possesses a number of the unusual properties, originally described in detail by prof. Hosono [1]. Its structure is defined by the presence of the cationic framework $[Ca_{24}Al_{28}O_{64}]^{4+}$, while the electroneutrality of the whole structure is established by the anionic lattice $4X^-$. For mayenite obtained under oxidizing conditions, the most typical sublattice anions, in addition to the oxide anion O^{2-}, are radical oxygen species such as O^-, O_2^{2-}, O_2^-. Previously it was shown that the presence of such active species was beneficial while using mayenite as a catalyst support for volatile organic compounds oxidation and biomass tar steam reforming [2].

The most common way to synthesize such materials is a high-temperature solid-phase reaction between the corresponding oxides, but such a technique produces non-porous samples with very limited usability as catalysts and adsorbents. This problem can be dealt with by applying the aerogel technique, which is based on the alkoxide sol-gel method with subsequent removal of solvents under supercritical conditions in an autoclave. The practical elimination of the surface tension during the drying procedure results in preservation of the initial porous gel structure.

In this work calcium methoxide and aluminum isopropoxide dissolved in the mixture of corresponding alcohols were used as the precursors. The reaction mixture was subjected to hydrolysis, followed by drying in an autoclave at a temperature of 270 °C and a pressure of 80 atm. Such a method allowed us to obtain samples with specific surface area as high as 330 m^2/g after drying. The use of a five-fold excess of water (compared to the stoichiometric amount) led to the formation of the crystalline mayenite immediately after drying in an autoclave [3].

During the high temperature treatment fine metal oxide materials tend to lose their initial dispersity due to sintering. This issue can be solved by isolation of the individual particles in the material by creating a carbon shell on the surface of the oxide core [4]. In this work resorcinol, introduced into the reaction mixture prior to hydrolysis, was used as an organic precursor to create a carbon shell. After supercritical drying the samples were subjected to a heat treatment in an argon flow in order to obtain carbon coating during resorcinol pyrolysis. Such procedure yielded samples with specific surface area as high as 290 m^2/g after treatment at 1100 °C. According to the XRD data, the combustion of the carbon shell did not affect the phase composition of oxide core and therefore can be used for evaluation of the textural characteristics of the oxide core. Moreover, the carbon shell deposition was shown to efficiently stabilize the mayenite phase at 1100 °C. After treatment at 1100 °C in inert atmosphere with subsequent burnout of carbon sample with high resorcinol concentration retained the surface area as high as 72 m^2/g, which exceeded the surface area of the sample without shell after the same treatment by a factor of five.

We found that deposition of a carbon shell on the surface of calcium aluminate indeed leads to the stabilization of its textural properties and phase composition. Preservation of the oxide core dimensions at high calcination temperatures due to the effect of the carbon shell is a significant result. This method seems to be very promising for preparation of nanocrystalline mayenite with high surface area in the active form requiring heat treatment at very high temperatures.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation [project № FWUR-2024-0034].

References

1. Li Q., Hosono H., Hirano M., Hayashi K., Nishioka M., Kashiwagi H., Torimoto Y., Sadakata M., Surf. Sci., 2003, 527, 100–112.
2. Intiso A., Rossi F., Proto A., Cucciniello R., Rend. Lincei Sci. Fis. Nat., 2021, 32, 699–708.
3. Ilyina E.V., Gerus Y.Y., Cherepanova S.V., Bedilo A.F., Mater. Lett., 2021, 293, 129699.
4. Volodin A.M., Bedilo A.F., Stoyanovskii V.O., Zaikovskii V.I., Kenzhin R.M., Mishakov I.V., Vedyagin A.A., RSC Adv., 2017, 7, 54852.

CuO-MnO_x-CeO_2-based catalysts for CO oxidation: effect of preparation method

N.V. Dorofeeva, A.S. Savel'eva, M.A. Baturo, M.V. Grabchenko, M.A. Salaev

National Research Tomsk State University, Tomsk, Russia

nv-dorofeeva@yandex.ru

Pollution of atmospheric air is a global environmental challenge requiring advanced approaches to reduce harmful emissions (CO, NO_x, SO_x, volatile organic compounds) from industrial enterprises and automobile vehicles. The main route to convert harmful compounds, including CO, into safer products is catalytic oxidation. High catalytic activity of the d-metal oxides is due to the relatively low energy required to change the valence, which facilitates electronic transitions when interacting with the reagents. Thus, mixed oxide catalysts based on less expensive transition metals and CeO_2 with high oxygen storage and release capacities are promising for CO oxidation [1, 2].

The purpose of this work was to reveal the effect of the method of Cu introduction to form CuO-CeO_2 and CuO-MnO_x-CeO_2 mixed oxides on their structure and catalytic properties in CO oxidation.

Copper-containing catalysts based on CeO_2 and $CeMnO_x$ were prepared by incipient wetness impregnation and one-pot synthesis. CeO_2 and $CeMnO_x$ as well as Cu-containing systems, i.e., $CuCeO_x$ and $CuCeMnO_x$, were obtained by solvothermal synthesis in ethylene glycol. Supported Cu/CeO_x and $Cu/CeMnO_x$ catalysts were obtained by impregnating of ceria and cerium-manganese oxides. The amount of Cu in all samples was 2 wt.%. The compositions of the oxides were determined by XRF, XRD and Raman spectroscopy methods. The textural properties of the oxides were studied by low-temperature nitrogen adsorption. The redox properties were estimated by TPR-H_2. The CO oxidation reaction was carried out in the reaction mixture of 1% CO/5% O_2/He on the AutoChem device (Micromeritics, USA) equipped with the gas mass spectrometer UGA-300.

All catalysts feature a mesoporous structure and high specific surface areas from 52 to 94 m^3/g. According to the XRD data, only a fluorite-type phase with the CSR of 5-12 nm is observed for all catalysts. The Mn introduction into the system leads to the formation of particles with smaller crystallite sizes. In the Raman spectra of Mn-containing samples, the Ce-O absorption band (464 cm^{-1}) is shifted towards lower wave numbers, which indicates the formation of solid solutions of Ce-Mn oxides on the surface of CeO_2 particles. The shift of the Ce-O vibrational band for the Cu/CeO_x and $CeCeO_x$ is less noticeable. The absorption band at 600-650 cm^{-1} observed for all catalysts is associated with the presence of bulk oxygen vacancies. The TPR-H_2 method established the presence of copper in the catalysts in several states: highly dispersed CuO particles strongly interacting with the support, CuO clusters and Cu^{n+} in the $Cu_xCe_{1-x}O_{2-\delta}$ solid solution.

The introduction of both manganese and copper leads to a significant decrease in the CO oxidation temperature: $T_{50\%}$ for the studied catalysts varies from 80 to 139 °C. It is noteworthy that in the case of catalysts obtained by the solvothermal method, the CO oxidation temperatures are lower than for the catalysts obtained by impregnation. The lowest temperature of CO oxidation, $T_{50}\% = 80$ °C, was obtained for the $CuCeO_x$ sample prepared by solvothermal method.

This work was supported by the Russian Science Foundation, Grant № 23-73-00109.

References

1. Grabchenko M.V., Mamontov G.V., Chernykh M.V., Vodyankina O.V., Salaev M.A., Chem. Eng. Sci., 2023, 285, 119593.
2. Grabchenko M.V., Mikheeva N.N., Mamontov G.V., Cortés Corberán V., Litvintseva K.A., Svetlichnyi V.A., Salaev M.A., Nanomaterials, 2023, 13, 3108.

Catalytic systems based on SAPO-11 nanoscale molecular sieves - new opportunities for the isodeparafinization of fuels and oils

D.V. Serebrennikov[1], R.E. Yakovenko[2], I.N. Zubkov[2], D.O. Bagdanova[1], A.R. Zabirov[1], G.T. Bagautdinova[3], R.Z. Kuvatova[1], B.I. Kutepov[1], M.R. Agliullin[1]

[1]*Institute Petrochrmistry and Catalysis UFRC RAS, Ufa, Russia*
[2]*Platov South-Russian State Polytechnic University (NPI), Novocherkassk, Russia*
[3]*Ufa State Petroleum Technical University, Ufa, Russia*

d25c25@yandex.ru

SAPO-11 are the most promising materials for creating bifunctional catalysts for hydroisomerization of high C_{16}+ paraffins due to their one-dimensional channel porous structure with a pore size ~5 Å and "moderate" acid centers. These materials are used for isodewaxing of diesel fuels and oils [1]. Despite certain successes in their synthesis and application, the problem of diffusion limitations remains unsolved. Solving this problem would allow for higher activity, selectivity, and stability of catalytic systems based on these materials [2]. To reduce diffusion limitations, various methods for synthesizing nanoscale SAPO-11 have been proposed, but most of them rely on the use of crystal growth modifiers.The main disadvantages of these methods are their high cost and the reduced degree of crystallinity of the materials produced, which makes it difficult to implement them on an industrial scale.

The aim of this research is to develop novel methods for the synthesis of SAPO-11 nanoscale molecular sieves without the use of various crystal growth modifiers. This paper presents the results of our efforts to synthesize SAPO-11 using a novel approach that involves the crystallization of silicoaluminophosphates from reaction gels containing a high concentration of crystal-forming components, as well as the use of nanoscale SiO_2 sol. The materials obtained were characterized using a range of techniques, including XRF, STEM, TEM-SAED, MAS NMR, low-temperature nitrogen adsorption-desorption N_2, IR spectroscopy of probe molecules (pyridines) and TPD-NH_3

It was shown for the first time that, depending on the aluminum source used, the methods presented in this work allow the crystallization of SAPO-11 with a nanoscale or hierarchical porous structure, with crystal sizes ranging from 50 to 200 nanometers. These materials have a S_{BET} of 260-310 m^2/g, a V_{micro} from 0.08 to 0.12 cm^3/g, V_{meso} from 0.2 to 0.35 cm^3/g, and V_{macro} from 0.4 to 0.5 cm^3/g. The total acidity of NH_3 of these materials ranges from 250 to 600 µmol/g.

Hierarchical and nanoscale samples of Pt/SAPO-11 were studied in the hydroisomerization reactions of n-hexadecane, diesel fractions, and GTL wax. These samples showed higher activity and selectivity in these transformations compared to microporous silicoaluminophosphate samples.

This work was supported by the state assignment of the UFRS IPC RAS (№FMRS-2024-0012 "Molecular sieve bifunctional catalytic systems for the production of winter and arctic diesel fuels").

References

1. Wei W., et al. Catal. Sci. Technol., 2019, 9, 4162.
2. Agliullin M.R., et al. (A Review). Pet. Chem., 2021, 61, 852–870.

Synthesis of sulfated Al_2O_3 aerogels and study of their catalytic activity in ethanol dehydration

E.I. Shuvarakova[1], A.F. Bedilo[1], A.E. Riznitsky[2], A.S. Miliushina[1,2]

[1]Boreskov Institute of Catalysis, Novosibirsk, Russia
[2]Novosibirsk State Technical University, Novosibirsk, Russia

katerina.shuv@gmail.com

It is known that the deposition of sulfates on the surface of γ-Al_2O_3 leads to a significant increase in its acidity and catalytic activity in acid-catalysed reactions. The catalytic properties of sulfated alumina are generally similar to those of sulfated zirconia, which is more widely known for its higher acidity and catalytic activity. However, its low cost, high specific surface area, availability and thermal stability make sulfated alumina an attractive catalyst for processes catalysed by medium strength acid sites [1].

The term aerogel refers to gel-like materials in which the liquid phase is replaced by a gas. Under normal conditions, drying leads to the destruction of the porous structure of the original gels. However, under conditions of supercritical pressure and temperature, the structure does not collapse. An important property of aerogels is their high specific surface area, which provides a large number of active sites per unit mass, making them suitable for use in catalysis [2].

To prepare aluminium oxide aerogels, a solution of aluminium isopropoxide in isopropanol was subjected to hydrolysis with a stoichiometric amount of water, followed by stirring for 24 h and drying in an autoclave at 265 °C. The results of XRD analysis showed that the obtained aerogels were amorphous. Their specific surface area after calcination in air at 550 °C was 450 to 500 m^2/g, which is about 2 times higher than that of catalysts prepared by conventional methods. The sulfated aluminium oxide samples were prepared by incipient moisture impregnation of the obtained aerogels and by introducing sulfuric acid at the gel preparation stage. The introduction of sulfuric acid resulted in a decrease in pore volume, while the high specific surface area of the Al_2O_3 aerogels did not significantly change. Also, samples of commercial Al_2O_3 with different amounts of deposited sulfates were prepared by impregnation method for comparison.

The obtained samples of sulfated aluminium oxide were studied in the ethanol dehydration reaction. The sample was activated in argon flow at 300°C for 30 min, then the flow was switched to a bubbler with ethanol and the reaction was carried out at the same temperature. The reaction products were analysed using a gas chromatograph.

The samples obtained by the moisture impregnation method showed a tendency to increase the total ethanol conversion and ethylene yield with increasing concentration of deposited sulfates. Thus, the conversion and ethylene yields were 23% and 5%, respectively, on pure aluminium oxide and 82% and 75% on the sample containing 12% SO_3.

The samples obtained by the aerogel method by introducing sulfuric acid at the gel synthesis stage showed practically no change in total conversion and ethylene yield with increasing sulfate concentration. The total conversion of all samples was about 70%, but the yield of diethyl ether was almost twice that of ethanol. The sample obtained by impregnation of pure Al_2O_3 aerogel with sulfuric acid solution shows the highest ethylene yield of 79.9%.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the governmental assignment for Boreskov lnstitute of Catalysis (project FWUR-2024-0034).

References

1. Bedilo A.F., Shuvarakova E.I., Rybinskaya A.A., Medvedev D.A., J. Phys. Chem. C, 2014, 11815779.
2. Ilyina E.V., Bedilo A.F., Cherepanova S.V., Gerus Y.Y., Shuvarakova E.I., Vedyagin A.A., J. Sol-gel Sci Technol., 2022, 104, 259.

The hydrolysis of sodium borohydride over solvent-free synthesized cobalt-containing catalysts

D.A. Sukhorukov, K.A. Dmitruk, S.A. Mukha, O.V. Komova, V.I. Simagina, O.V. Netskina

Boreskov Institute of Catalysis, Novosibirsk, Russia

sukhorukov@catalysis.ru

Nowadays there is a necessity to create advanced technologies for compact hydrogen storage in portable energy devices based on fuel cells. Taking into account a high hydrogen capacity, a chemically-bonded form of hydrogen such as sodium borohydride is of primary interest [1]. Water addition to this hydride immediately leads to the H_2 generation according to the following reaction:

$NaBH_4 + 4H_2O \rightarrow NaB(OH)_4 + 4H_2\uparrow$.

In the presence of catalysts this process can be carried out even at negative ambient temperatures, making the hydride interesting for H_2 production in Russian different climatic conditions. Among other catalysts, a specific attention is paid towards systems with Co_3O_4, as they possess high activity and stability in the hydrolysis of $NaBH_4$ [2]. Recently, we have noted [3] that the synthesis method influences the catalytic properties of cobalt oxide. Developing this tendency and taking into account the principles of Green Chemistry, we propose a new approach based on a solvent-free synthesis of cobalt catalysts by a solid-state combustion (SSC) of cobalt-organic complexes. The complex compounds contained energy-rich N-containing ligands (imidazole, pyrazole, and ethylenediamine) and nitrate- or perchlorate-anions as oxidizers. The formation of the complexes under study was confirmed by ATR-FTIR, XRD, etc.

The synthesized cobalt complexes were heated in the air above the critical temperature of the thermal explosion to initiate their gasification with the formation of highly-dispersed condensed phase, i.e. cobalt oxide particles [4]. The mechanism of SSC was described by thermal analysis.

The obtained samples were tested in the hydrolysis of $NaBH_4$, the kinetics of the process was investigated with temperatures range of 20-60 °C. It was shown that initially there was an induction period with slow hydrogen generation. At this stage there was a cobalt reduction with the formation of active catalyst phase. The duration of this stage was defined by the cobalt state, depending on the gasification conditions and the composition of the initial complex. After the activation, the rate of hydrogen evolution sharply rose, and the kinetics of the reaction was described by the zero order equation. At the same time the calculated values of activation energy were similar for all samples tested, in spite of the different rate of H_2 generation. It should be noted that all of the catalysts, synthesized by SSC, were characterized by a higher activity, compared to the commercial Co_3O_4. Thus, we have demonstrated the perspective of this approach to the synthesis of Co-containing catalysts from energy-rich complexes to obtain hydrogen by the catalytic hydrolysis of $NaBH_4$.

The authors are deeply grateful to Bulavchenko O.A., Prosvirin I.P., Pochtar A.A., Shmakov A.G., Paletsky A.A. for the comprehensive assistance in this research. This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the framework of the state assignment of the Boreskov Institute of Catalysis SB RAS (the project FWUR-2024-0034).

References

1. Abdelhamid H.N., Int. J. Hydrogen Energy, 2021, 46, 726–765.
2. Edla R., Gupta S., Patel N., Bazzanella N., Fernandes R., Kothari D. C., Miotello A., Appl. Catal. A Gen., 2016, 515, 1–9.
3. Simagina V.I., Ozerova A.M., Komova O.V., Odegova G.V., Kellerman D.G., Fursenko R.V., Odintsov E.S., Netskina O.V., Catal. Today, 2015, 242 (Part A), 221–229
4. Komova O.V., Mukha S.A., Ozerova A.M., Bulavchenko O.A., Pochtar A.A., Ishchenko A.V., Odegova G.V., Suknev A.P., Netskina O.V., Nanomaterials, 2021, 11 (12).

On notable effect of graphene oxide surface on catalytic activity of Ag/graphene oxide catalysts in nitroarene reduction

A.V. Taratayko, G.V. Mamontov

Tomsk State University, Tomsk, Russia

taratayko1997@mail.ru

Graphene oxide (GO) is a carbon material derived from layered graphite structure via oxidative treatment. Optical, thermo-, and electroconductive properties allow utilizing the GO as an advanced material for electrodes and photoactive coatings in electronics [1]. Moreover, abundant oxygen-containing moieties facilitate using this material in water medium. This provides employment of the GO in biomedicine for biocompatible composites, biosensors, membranes, and drug delivery, and in ecological adsorption processes especially toward polar compounds [2, 3]. In addition, GO application in catalysis as a support is in up-to-date research focus [2, 4]. Despite a significant number of research papers devoted to GO-based catalysts, a minor attention is paid to an influence of the GO surface state on distribution and state of an active component and, as a result, catalytic properties of on-based catalysts. This work aims to demonstrate an effect of the GO unmodified surface or modified one with CeO_2 on catalytic activity of deposited Ag species in a nitroarene model reaction.

The GO was synthesized by oxidative treatment of graphite powder via modified Hummers method. A series of Ag-containing catalysts were synthesized by the GO impregnation method with $AgNO_3$ solution at pH 11 (Ag/GO) and with $Ce(NO_3)_3$ addition (Ag-CeO_2/GO) or at pH 5 without any modifier (Ag/GO_pH5). A part of the GO, which was treated with NH_3 solution, was used as a comparison sample. The samples were characterized by physicochemical methods: XRD, TG-DSC, SEM, HR TEM, UV-visible spectrometry, etc. Catalytic properties of the catalysts were tested in 4-nitrophenol reduction into 4-aminophenol by $NaBH_4$ at room temperature and atmospheric pressure in water medium.

The GO microstructure demonstrates thin sheets of folded carbon layers (7-8 layers regarding the XRD calculations), which are organized in “crumpled paper” particles sized of several micrometers (SEM data). According to the XRD and TG-DSC data, the GO structure and composition undergo changes upon pH increase: a decrease of weight loss step occurs at 200-250 °C due to a partial elimination of functional groups in alkaline medium, and a broad XRD peak occurs at ~25° 2θ that is attributed to substantially disordered carbon layers of partially reduced GO. Lack of functional groups leads to a dramatic decrease of the catalytic activity in 4-nitrophenol reduction of the Ag/GO sample (k = 1.62 min^{-1}) in contrast to the Ag/GO_pH5 one (k = 7.43 min^{-1}) that retains the most of functional groups at pH 5. Therefore, polar functional groups on the GO surface stabilize dispersed and evenly distributed (regarding the HR TEM data) active Ag nanoparticles. The role of CeO_2 nanoparticles as a modifier is being additional sites to stabilize Ag species onto the GO surface at pH 11 and increase the catalytic activity in 4-nitrophenol reduction from k = 1.62 min^{-1} to k = 3.77 min^{-1} for Ag-CeO_2/GO sample.

Thus, the state of the GO surface significantly affects the catalytic activity of Ag-containing catalysts in 4-nitrophenol reduction into 4-aminophenol. Sufficient polar functional groups on the GO surface and CeO_2 nanoparticles as a modifier stabilize active nanosized species of metallic silver.

This work was funded by the State assignment of the Ministry of Education and Science of the Russian Federation (project No. FSWM-2020-0037).

References

1. Singh R.K., Kumar R., Singh D.P., RSC Adv., 2016, 6, 64993–65011.
2. Yadav S., Raman A.P.S., Meena H., Goswami A.G., et al., ACS Omega, 2022, 7, 35387–35445.
3. Yusuf M., Kumar M., Khan M.A., Sillanpa M., Arafat H., Adv. Colloid Interface Sci., 2019, 102036.
4. Prasad C., Liu Q., Tang H., Yuvaraja G., Long J. Rammohan A., Zyryanov G.V., J. Mol. Liq., 2019, 111826.

Modifying effect of cobalt in Pd-Co/α-Al_2O_3 catalysts for selective hydrogenation of acetylene to ethylene

D.V. Yurpalova[1], T.N. Afonasenko[1], Z.S. Vinokurov[2], I.P. Prosvirin[3], A.V. Bukhtiyarov[3], M.V. Trenikhin[1]

[1]Center of New Chemical Technologies BIC, Boreskov Institute of Catalysis, Omsk, Russia
[2]Synchrotron Radiation Facility SKIF, Boreskov Institute of Catalysis, Koltsovo, Russia
[3]Boreskov Institute of Catalysis, Novosibirsk, Russia

omsk-glyzdova@mail.ru

Catalysts containing bimetallic Pd-Co particles are widely used. For example, Pd-Co systems have been successfully applied in the processes of selective hydrogenation of various substrates [1, 2]. It is worth noting that the number of studies related to the use of Pd-Co catalysts in the practically important reaction of acetylene hydrogenation to ethylene [3, 4] is very limited, despite the fact that this process is necessary to obtain pure ethylene, which is widely used in petrochemistry for the synthesis of valuable products. The purpose of this work was to study the modifying effect of Co on Pd in Pd-Co/α-Al_2O_3 catalysts, as well as to establish relationships between the catalyst composition, the state of the active component and the properties of the samples in the reaction of acetylene hydrogenation to ethylene.

Al_2O_3 (Sasol) calcined in air at 1200°C in the form of α-modification ($S_{BET} = 5$ m^2/g) was used as a catalyst support. The catalysts were synthesized by incipient wetness impregnation method with aqueous solution of palladium and cobalt nitrates. The samples were dried at 120°C and reduced in H_2 at 400 – 700°C. The Pd content in all catalysts was 0.5 wt.%. The Pd/Co molar ratio was varied from 1/0.5 to 1/4. The state of the active component was studied by XRD, XPS, TPR-H_2 and TEM methods. Hydrogenation of C_2H_2 was carried out in flow mode at 25-95°C. The reaction mixture included 4 vol.% of C_2H_2 in H_2.

An increase in the reduction temperature of Pd-Co/α-Al_2O_3 catalysts (Pd/Co molar ratio is 1/2) in H_2 from 400 to 700°C leads to a decrease in activity, but a significant increase in ethylene selectivity (from 47% to 63% at 95°C), which is associated with the formation of $Pd_xCo_{(1-x)}$ solid solution particles in the samples. An increase in the reduction temperature leads to the enrichment of bimetallic particles with cobalt: according to X-ray diffraction data, a sample reduced at 400°C contains the $Pd_{0.76}Co_{0.24}$ phase, while reduction at 700°C is accompanied by the formation of the $Pd_{0.58}Co_{0.42}$ phase with a higher modifier concentration. The binding energy (BE) of Pd3d$_{5/2}$ in the Pd-Co sample reduced at 700°C is 335.3 eV, which is 0.4 eV higher than BE for Pd in Pd/α-Al_2O_3. An increase in the amount of Co to Pd/Co = 1/3 leads to a shift of BE of Pd3d$_{5/2}$ to 335.5 eV, while a further introduction of cobalt to Pd/Co = 1/4 does not affect the electronic state of Pd. The catalytic properties of the samples correlate well with the electronic state of Pd: changing of Pd/Co from 1/0.5 to 1/3 leads to a decrease in activity with an increase in selectivity to 69%. In this case, an increase in the Co content to Pd/Co = 1/4 is accompanied by stabilization of the catalytic characteristics. According to XRD, up to the ratio Pd/Co = 1/3 the concentration of Co in Pd-Co particles increases to ~59 at.% and adding more Co to Pd/Co = 1/4 leads to the formation of two phases – one enriched in palladium $Pd_{0.57}Co_{0.43}$ and a cobalt phase including an impurity of palladium $Pd_{0.13}Co_{0.87}$. It is assumed that higher selectivity in the acetylene hydrogenation reaction is ensured by the action of $Pd_xCo_{(1-x)}$ particles containing an excess amount of Co relative to Pd. The similar characteristics of Pd-Co/α-Al_2O_3 catalysts with Pd/Co = 1/3 and 1/4 can be explained by the additivity of the action of the bimetallic phases present in the catalyst with the molar ratio Pd/Co = 1/4.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the governmental assignment for Boreskov lnstitute of Catalysis (project FWUR-2024-0039).

References

1. Yoshii T., Nakatsuka K., Kuwahara Y., Mori K., Yamashita H., RSC Adv., 2017, 7, P.22294–22300.
2. Li X., Zhu X., Ren Z., Si X., Lu R., Lu F., ChemNanoMat., 2022, 8, e202200059.
3. Ma R., Yang T., Sun J., He Y., Feng J., Miller J.T., Li D., Chem. Eng. Sci., 2019, 210, 115216.
4. Yurpalova D.V., Afonasenko T.N., Prosvirin I.P., Bukhtiyarov A.V., Kovtunova L.M., Vinokurov Z.S., Trenikhin M.V., Gerasimov E.Yu., Khramov E.V., Shlyapin D.A., J. Catal., 2024, 432, 115417.

Dry reforming of methane over Ni/CeO_2-SnO_2: effect of the Ni addition method

A.A. Zorina, I.Yu. Kaplin, E.S. Lokteva, A.N. Kharlanov

Department of Chemistry, Lomonosov Moscow State University, Moscow, Russia

annazaria47@mail.ru

Dry reforming (DRM) is a very promising method of reducing the environmental risks associated with GHG emissions [1]. Ni catalysts considered to be an alternative to high-cost noble metal systems, but they are prone to rapid deactivation. Control of Ni particle size and metal-support interaction strength play a key role in synthesis of highly efficient Ni catalysts for DRM. This work was aimed at elucidation of the effect of the Ni addition method on catalytic properties of Ni/CeO_2-SnO_2 in DRM.

Ceria-tin (CeSn) oxide catalytic systems were synthesized using Pluronic 123 (P123) as organic template and aqueous solutions of $Ce(NO_3)_3 \cdot 6H_2O$ and $SnCl_2 \cdot 2H_2O$ as precursors. Ni (9wt.%) was applied on oxide support using wet impregnation (WI) and deposition-precipitation (DP) methods from aqueous solution of $Ni(NO_3)_3 \cdot 6H_2O$. We also synthesized nickel-ceria-tin systems (9wt.%Ni) from salts aqueous solutions using co-precipitation (CP) method. All systems were calcined at 800°C. All catalysts (0.1g) were reduced in 10 vol.% H_2/N_2 for 1h at 750°C before catalytic tests. The catalysts were tested in DRM at 800°C using a flow reactor and a reaction mixture $CH_4/CO_2/N_2$=1/1/2 (F_0=30 ml/min). The reaction products and unconverted reagents were analyzed by online gas chromatography Chromatec-Crystal 5000.2 (“Chromatec”, Russia) with Carboxen-1010 PLOT column (“Supelco”, USA).

All systems were active in DRM. 9WI system showed the highest stationary conversion of both reagents ($X(CH_4) = 32\%$, $X(CO_2) = 51\%$) compared to 9CP ($X(CH_4) = 26\%$, $X(CO_2) = 45\%$) and 9DP ($X(CH_4) = 18\%$, $X(CO_2) = 36\%$). We interrupted the catalytic test without unloading the reactor and continued it the next day. Only impregnated catalyst was notably deactivated: $X(CH_4) = 26\%$, $X(CO_2) = 45\%$. According to ex situ XPS 9WI and 9DP have similar Ce/Ni ratio equal to 0.46 and 0.51, resp. For 9CP this value is significantly higher (Ce/Ni=2.75) indicating Ni(II) species concentrate in volume. Although in both 9WI and 9DP active metal locates on the surface, the addition of Ni by DP method led to the formation of larger metal particles with weak Ni-support interaction. It was also confirmed by TPR-H_2. The presence of such Ni species resulted in slightly lower catalytic activity for this system. TEM confirmed the existence of 17–19 and 5–7 nm Ni particles in 9DP and 9WI, resp. Individual Ni particles were almost not visible on the surface of 9CP. The use of co-precipitation method led to the generation of NiO species in the support volume and possibly the formation of mixed nickel-cerium-tin oxide phase. Such strong metal-support interaction resulted in lower catalytic activity, but improved resistance towards deactivation. We also tested systems after catalysis (350 min in DRM) in order to identify the evolution of active phase during DRM. According to the Raman spectroscopy the ratio value of intensities of I_D/I_G modes was less for 9WI. It showed the more graphitized carbon is formed on the surface of impregnated sample. It was also confirmed by TG-DTA, the maximum of exothermic process (oxidation of carbon) was higher for impregnated sample and also only 9WI showed decrease of mass (2.5%). Ni species formed by impregnation method were the most active in DRM. Slight deactivation could have been caused by high activity of this system in comparison to others. More detailed reasons of 9WI deactivation will be discussed in the report.

We also tested Ni/CeSn-P123 systems prepared by using different nickel salts (acetate, acetylacetonate) in order to study the correlation of precursor nature with size and dispersion of formed metal species and their interaction strength with the surface. Additionally, detailed studies using FTIR CO, XRD, SEM-EDX, low-temperature nitrogen adsorption-desorption methods revealed the influence of state of the Ni particles on the surface, textural and morphological characteristics of the resulting systems, on their activity and stability in the DRM reaction.

The work was carried out using scientific equipment purchased under Lomonosov Moscow State University development programme.

References

1. Alhassan A. et al., Journal of Cleaner Production, 2023, 138638.

New prospective precursors for preparation effective catalysts CrO_x-ZrO_2-SiO_2 and Pt/CrO_x-ZrO_2-SiO_2 for non-oxidative propane dehydrogenation

I.Yu. Kaplin, E.V. Golubina, A.V. Gorodnova, E.S. Lokteva

Department of Chemistry, Lomonosov Moscow State University, Moscow, Russia

kaplinigormsu@gmail.com

Unsaturated hydrocarbons especially ethylene and propylene are the main feedstock for a wide range of polymer materials. One of the most promising methods for their production is the catalytic dehydrogenation of light paraffins, including propane [1]. The industrial dehydrogenation catalysts usually contain Pt or CrO_x particles supported on Al_2O_3. ZrO_2-based systems modified with silica and small amount of CrO_x as an active component are promising catalysts for non-oxidative propane dehydrogenation (PDH). The use of various zirconium and silica precursors, including metal-organic frameworks and biological materials, can also have a significant effect on the resulting structural and surface properties of catalysts, which requires more detailed study.

CrO_x-ZrO_2-SiO_2 and 1wt.% Pt/CrO_x-ZrO_2-SiO_2 catalysts were prepared using one-pot method with cetyltrimethylammonium bromide (CTAB) and TEOS as templates. The MOF-derived catalyst with the same composition were synthesized by pyrolysis of zirconium-based metal organic framework UiO-66 in the presence of Zr and Cr precursors and SiO_2 from rice husk in DMF (figure 1, (A)). The chromium loading was 6 wt%; the (Cr+Zr)/Si molar ratio was 0.8. All samples were calcined at 600°C in air for 4 h. The systems were denoted as CrZrSi, PtCrZrSi and CrSi/UiO-66, PtCrSi/UiO-66 respectively. 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 quartz reactor (100 mg). 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 was analyzed by GC Crystal-5000.2 (“Chromatec”, Russia) equipped with a HP-PLOT “Al_2O_3”-S capillary column (Agilent, USA) and a FID. The catalysts were characterized by H_2-TPR, XRD, Raman spectroscopy, XPS, FTIR, SEM-EDX, N_2 physisorption and DSC-TG.

The CrSi/UiO-66 catalyst showed the best catalytic efficiency at 500 and 550°C (figure 1) among non-platinum-modified systems. This sample has uniform distribution of Cr and Zr, which is consistent with the SEM-EDX. On the contrary, in the CrZrSi sample there are local areas of chromium accumulation. According to the H_2-TPR data, the H_2 uptake related to reduction of Cr^{+6} species is the most intensive for CrSi/UiO-66. Under reaction conditions the major part of Cr in the sample was easily reduced to active Cr^{3+} species. According to the XRD data the ZrSi support presents in the samples as highly dispersed crystalline particles. Long-term stability tests at 550°C led to the deactivation of catalysts due to the coke formation, but the CrSi/UiO-66 was more stable under PDH conditions. Raman spectra of the catalysts after 200 minutes in the reaction mixture contain lines related to carbon species and bands in the region of 500-800 cm^{-1} associated with Cr^{3+} oxides. For the CrZrSi and CrSi/UiO-66 samples there were no lines characteristic for Cr^{6+} compounds. It is important to note that the fraction of defective carbon is higher for CrSi/UiO-66, which explains the easier removal of coke deposits in this sample. Catalytic experiments with PtCrZrSi and PtCrSi/UiO-66 are currently underway.

The report will also present the data on regeneration treatment under various conditions and time intervals for all prepared systems after prolonged contact with the reaction mixture. The state of platinum in modified systems will be studied in detail based on TEM, XPS, FTIR-CO and TPR methods.

The research was supported by RSF (project No. 22-23-00445). Some scientific equipment was purchased using Moscow State University development program.

References

1. Sattler J.J.H.B., Ruiz-Martinez J., Santillan-Jimenez E., Weckhuysen B.M., Chem. Rev., 2014, 114, 10613–10653.

New approaches for the synthesis of M/C_g -type structures (M=Ni, Co, Cu) via microwave irradiation and their application in the electrocatalytic water splitting

V.S. Kashansky[1,2], A.V. Sukhov[1,2], A.V. Ivanov[3], A.M. Kuchkaev[1,2], T.B. Tkachenko[3],
D.G Yakhvarov[1,2]

[1]Alexander Butlerov Institute of Chemistry, Kazan Federal University, Kazan, Russia
[2]Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center of RAS, Kazan, Russia
[3]Kemerovo State University, Kemerovo, Russia

vladkashansky@gmail.com

The consumption of fossil fuels (coal, gas, oil) is rising steadily with the population growth, but their reserves are limited. However, the use of these fuels has a negative impact on the environment due to the high release of CO_2. One of the most urgent tasks is therefore to find alternative, clean energy sources, and one of the most promising candidates for this role is hydrogen. It produces no pollutants when burned and has a high gravimetric energy density [1].

The electrochemical water splitting is one of the perspective approaches for hydrogen production. Platinum-based catalysts are the most effective systems for electrocatalytic hydrogen evolution reaction (HER). Some catalytic systems based on transition metals have been developed as high effective alternatives to platinum-based systems due to their low cost, high efficiency and stability [2].

In this work, we propose to obtain electrocatalysts based on transition metal nanoparticles deposited on graphite (C_g). The synthesis of these catalytically active materials has been made using microwave irradiation under reduced pressure. We have obtained the systems with the following composition: Ni/SiO_2/C_g; Ni, Co/Al_2O_3/C_g; Ni, Cu/Al_2O_3/C_g; Co/Al_2O_3/C_g. These systems were characterized by X-ray diffraction and transmission electron microscopy and their catalytic activity in HER under acidic and alkaline conditions have been studied.

This work was funded by the subsidy allocated to Kazan Federal University for the state assignment in the sphere of scientific activities, No.FZSM-2023-0020.

References

1. Zhu J., Hu L., Zhao P., Lee L.Y.S., Wong K.Y., J. Chem. Rev., 2020, 120 (2), 851–918.
2. Hu C., Lv C., Zeng N., Liu A., Liu Y., Hu L., et al., Energy Technol., 2023, 11 (1), 1–37.

Pd, Ag and Cu catalysts supported on biochar, prepared from pine nutshell, and its catalytic properties in 4-nitrophenol reduction

M.V. Kozhina, G.V. Mamontov

Tomsk State University, Tomsk, Russia

kozhina.milenav@yandex.ru

Recently, due to extensive exploitation and incorrect disposal of nitrophenol (4-NP), natural reservoirs and groundwater are polluted, which has a detrimental effect on the environment and human health [1]. Sorption and catalytic reduction of 4-NP are more promising technologies to solve this problem. Various noble metal catalysts have been developed for the reduction of 4-NP to respective 4-aminophenol (4-AP). However, due to their high cost and low availability, there is a need to replace them with base metals, among which copper is of great interest due to its low cost and large reserves in the earth's crust. Also, over the last decade, carbon materials have attracted significant attention in heterogeneous catalysis [2]. Therefore, in this work, biochar is proposed as a support due to its cost-effective production, convenient regeneration processes and the presence of a wide variety of surface functional groups. Now, supplies of the most used coconut coal have become difficult and expensive, so there is a need to develop coal from domestic raw materials (pine nut shells), which is not inferior in characteristics.

The purpose of this work is to develop methods for activating carbon material prepared from pine nut shells, synthesis of Pd, Ag and Cu catalysts based on it, study of the features of structure, sorption properties and catalytic activity of carbon material and catalysts based on it in the catalytic reduction of 4-nitrophenol into 4-aminophenol at room temperature and atmospheric pressure using $NaBH_4$ as reducing agent.

Pd, Ag and Cu-containing catalysts based on biochar, prepared from pine nut shells, were synthesized by adsorption impregnation with using $Pd(NO_3)_2$ $AgNO_3$ and $Cu(NO_3)_2$ as metal precursors. Then catalysts were dried at 120 °C and reduced with $NaBH_4$ aqueous solution at room temperature or in 10 % H_2/Ar flow at 300 °C (Ag/biochar and Pd/ biochar) or 350 °C (Cu/biochar catalyst). The carbon support and catalysts were studied by low-temperature N_2 adsorption, powder XRD, temperature programed reduction (TPR-H_2), TEM and tested in the catalytic reduction of 4-nitrophenol in aqueous solution.

It was shown that mild oxidative activation of biochar at 250-280 °C leads to rise surface area from 879 to 1147 m^2/g due to increased amount of both micro- and mesopores. According to XRD and TEM data, the reduction of Cu/biochar catalyst leads to reduction of $Cu(OH)_2$, CuO and Cu_2O into metallic Cu particles with size up to 20 nm. Ag/biochar catalyst is characterized by the presence of metallic silver from few nanometers up to 30 nm and reductive treatments does not significantly influent on the state of silver. No reflections of Pd-containing phases are observed for Pd/biochar catalyst which indicates on the distribution of palladium in a highly dispersed state. Only reduction of Pd/biochar catalyst by hydrogen at 300 °C leads to formation of metallic Pd particles with size up to 5 nm.

Ag/biochar catalyst is characterized relatively high catalytic activity ($k = 0.55$ min^{-1}, $E_a = 40.7$ kJ/mol), and reductive pretreatment does not influent on its activity ($k = 0.50$ min^{-1}). Pd/biochar catalyst is characterized with higher activity ($k = 0.69$ min^{-1}, $E_a = 26.9$ kJ/mol), but decreasing activity after reduction by H_2 was observed ($k = 0.45$ min^{-1}) that we attribute with agglomeration of highly dispersed Pd clusters into nanoparticles. The Cu/biochar sample has the highest catalytic activity ($k = 0.93$ min^{-1}, $E_a = 33.3$ kJ/mol), reductive treatment leads to significant growth of activity ($k = 5.88$ min^{-1}).

This study is supported by the State assignment of the Ministry of Education and Science of the Russian Federation (project No. FSWM-2020-0037).

References

1. Chen Q., Ma C., Duan W. et al., Journal of Cleaner Production, 2020, 271, 122550.
2. Serp P., Machado B., Cambridge : Royal Society of Chemistry, 2015, 23, 555.

The effect of synthesis methods on catalytic properties of Ag/FeO_x catalysts in 4-nitrophenol reduction

T.A. Kuznetsov, M.V. Kozhina, A.V. Taratayko, G.V. Mamontov

Tomsk State University, Tomsk, Russia

taratayko1997@mail.ru

Nowadays, nitroaromatic compounds are widely utilized in chemical industry as intermediate compounds for organic synthesis. However, nitroarenes are toxic and carcinogenic pollutants, and their catalytic reduction to aminoarenes is a promising removal method [1]. Noble metal-containing catalysts, including Ag-based ones, have proven to be advantageous in solving this problem [2]. Among a variety of iron oxides, the phases such as magnetite Fe_3O_4 and maghemite γ-Fe_2O_3 are of scientific interest due to ferrimagnetic properties that allow on-based catalyst extraction from reaction medium using magnetic field [3]. Thus, ferrimagnetic and low-toxic iron oxides are promising in environmental catalytic processes of nitrophenol reduction in aqueous solutions. This work aims to study the effect of synthesis methods on catalytic properties of Ag/FeO_x systems in 4-nitrophenol reduction reaction.

The γ-Fe_2O_3 support was synthesized by coprecipitation of Fe^{2+} and Fe^{3+} ions with aqueous ammonia solution. Ag/FeO_x composites were synthesized by co-precipitation of Fe^{2+} and Fe^{3+} ions with $[Ag(NH_3)_2]^+$-containing aqueous NH_3 solution, as well as by wetness impregnation of freshly prepared or pre-reduced in H_2/Ar flow Fe_2O_3 support with Ag^+ or $[Ag(NH_3)_2]^+$ solutions. The samples were characterized by physicochemical methods: XRD, TPR-H_2, low-temperature nitrogen adsorption-desorption, etc. Catalytic properties of the catalysts were tested in 4-nitrophenol reduction into 4-aminophenol with $NaBH_4$ at room temperature and atmospheric pressure in aqueous medium.

The synthesis approaches allow obtaining of a micro-mesoporous γ-Fe_2O_3 support with specific surface area of ~120 m^2/g that decreases to ~65–90 m^2/g upon silver deposition. According to the X-ray diffraction data, γ-Fe_2O_3 phase with particle size of ~10 nm is formed as the support. As for silver deposited by impregnation and co-precipitation, nano-sized metallic silver paerticles (sized up to 25 nm) are formed. The TPR-H_2 method demonstrates an interaction between iron oxide and deposited silver particles: joint reduction of Ag^+ to Ag^0 and γ-Fe_2O_3 to Fe_3O_4 occurs at 150–250 °C due to spillover of active hydrogen from silver to iron oxide, while γ-Fe_2O_3 to Fe_3O_4 transition occurs at 250–350 °C for pristine support.

It was shown that Fe_2O_3 support is not active in the reduction of 4-nitrophenol. The rate constant in 4-nitrophenol reduction for Ag/Fe_2O_3 catalysts was from 0.45 to 2.63 min^{-1}. The Ag/Fe_2O_3_pre-red.250(Ag^+) catalyst, prepared by impregnation of pre-reduced at 250 °C Fe_2O_3 support with $AgNO_3$ solution, demonstrates the superior activity due to efficient in-situ reduction of ionic silver into active dispersed metallic nanoparticles deposited on FeO_x surface. However, the Ag/Fe_2O_3_co-prec. catalyst, prepared by co-precipitation method, demonstrates the minor activity due to lower active Ag surface and incorporation of Ag species into FeO_x matrix. In addition, the possibility of catalysts separation from reaction mixture by using magnet was demonstrated.

Thus, the catalytic activity is affected by distribution and state of Ag species in the catalysts, which depends on synthesis methods. According to 4-nitrophenol reduction into 4-aminophenol in aqueous medium at room temperature and atmospheric pressure, impregnation of γ-Fe_2O_3, pre-reduced at 250 °C, with Ag^+ solution is the method to prepare the most active catalyst in the synthesized series.

This work was supported by the Russian Science Foundation, Grant № 23-73-10152.

References

1. Zhang K., Suh J.M., Choi J.-W., Jang H.W., Shokouhimehr M., Varma R.S., ACS Omega, 2019, 4, 483–495.
2. Orlandi M., Brenna D., Harms R., Jost S., Benaglia M., Org. Process Res. Dev., 2018, 22, 430–445.
3. Qu J., Ren C., Dong Y., Chang Y., Zhou M., Chen X., Chem. Eng. J., 2012, 211–212, 412–420.

Synthesis and study of UiO-66/PET and UiO-66/cotton composite sorbents

V.V. Lobanova, G.V. Mamontov

Tomsk State University, Tomsk, Russia

valeriialobanova@stud.tsu.ru

Metal-organic frameworks (MOFs) in recent years have attracted significant attention due to their unique properties, such as high specific surface area, tunable pore architecture, and high porosity, which are favorable for many current applications including gas storage and separation, catalytic processes, and purification. Most MOFs demonstrate low stability, limiting their application. UiO-66 exhibits unprecedented thermal (up to 500°C) and chemical stability [1]. UiO-66 consists of zirconium-oxygen clusters $Zr_6O_4(OH)_4$ connected by terephthalate linkers into a three-dimensional cubic framework, allowing for a branched spatial structure with a large specific surface area (1100-1800 m^2/g) and pore volume (0.40-0.90 cm^3/g) depending on the degree of defects.

However, all MOFs, including UiO-66, have a powdery state, significantly narrowing their field of application. The solution to this is the synthesis of composite materials in which MOF is stabilized on the surface of primary inorganic, organic or polymer support. This study is dedicated to the synthesis of the metal-organic framework Zr-UiO-66 on the surface of woven materials: polyethylene terephthalate (PET) and cotton.

Metal-organic framework UiO-66 was synthesized by a solvothermal method using HCl as a modulator. $ZrO(NO_3)_2 \cdot nH_2O$ was used as precursor of Zr^{4+}, terephthalic acid (BDC) as a ligand. $ZrO(NO_3)_2 \cdot nH_2O$ was dissolved in N,N-dimethylformamide (DMF) with HCl at 80°C. Terephthalic acid was dissolved in DMF under the same conditions. Afterwards, solutions were mixed and kept with stirring and heating for 1 hour. Then the resulting suspension was transferred to a steel autoclave to carry out at 120°C for 24 hours. Subsequently, the sample was washed in the 4th stage: twice 12 hours in DMF, 12 hours in alcohol and 8 hours in acetone [2]. Then composites were dried at 60°C under vacuum overnight. UiO-66 has been immobilized onto the surface of fabrics such as PET and cotton with using impregnation of fabric with zirconia precursor and assembly of UiO-66 in DMF solution containing BDC.

Porous structure of the synthesized UiO-66 was investigated by low-temperature N_2 adsorption. The prepared UiO-66 sample has a highly ordered porous structure with a developed specific surface area of 1200 m^2/g and pore volume of 0.41 cm^3/g. Micropores with a size of up to 2 nm predominate. In addition, the sample was examined by powder X-ray diffraction (XRD). The diffractogram clearly shows the reflexes corresponding to the phase of the UiO-66 at $2\theta \approx 7.3°$ and 8.5°.

The successful formation of the Zr-UiO-66 phase on the surface of PET and cotton was confirmed by the study of low-temperature N_2 adsorption, X-ray diffraction analysis and IR-Fourier spectroscopy. It is shown that the obtained composites have a specific surface area of 44 and 86 m^2/g respectively. The presence of pores of two sizes was demonstrated: micro- and meso-. As well as the presence of reflexes at 7.3° at 2θ on X-ray diffraction analysis, confirm the formation of UiO-66 on the surface of the tissue. The UiO-66 content on the surface of the fabric was 4 and 7 wt.% respectively.

Thus, it was shown that UiO-66 may be immobilized into PET and cotton. The localization of MOF on the surface of tissues was confirmed by an increase in the specific surface area of the resulting composite materials compared to the surface without MOFs. X-ray diffraction analysis and IR-spectroscopy confirms the formation of UiO-66 on the surface of PET and cotton.

This work was supported by the Tomsk State University Development Programme (Priority-2030, project № 2.4.5.24).

References

1. Cavka J.H., et al., J. Am. Chem. Soc., 2008, 130, 13850–13851.
2. Timofeev K.L., Kulinich S.A., Kharlamova T.S., Molecules, 2023, 28, 3916.

MOFs composites for adsorption organic compounds

P.A. Matskan, G.V. Mamontov

Tomsk State University, Tomsk, Russia

pmackan2002@gmail.com

Porous materials are used in many industrial applications. Their main application is sorption, catalysis, both for cleaning the environment from various pollutants and for obtaining target products. Classical porous material such as aluminum oxide, silica, carbon materials and others are usually amorphous porous solids that characterized by an unidentified structure, irregular pores and generally unfavorable for understanding structure-property relationships [1].

The distinctions of metalorganic frameworks (MOFs) from classical sorbents and catalysts are the hybrid organic-inorganic porous structure, that can be varied with a choice of a metal precursor, an organic linker and a way of modification. A high specific surface area (1000-3000 m^2/g) and a structural homogeneity provide an effective adsorption capacity and selectivity of MOFs. However, despite the above advantages, MOFs microporous structure embarrasses a mass transfer and limits an application of MOFs in processes linked to large molecules moving [2]. In addition, because of their fragility and fine crystalline powder form, MOFs industrial application is very difficult [3].

One of the ways deciding of these problems is creating of composite materials, where a MOF has a chemical or physical bond with the solid surface of a support as silica, carbon fiber, different natural and synthetic fabrics etc. The development of composite materials allows both to save microporous functions and to minimize diffusion limitation during delivering of large molecules to MOF's active centers.

Thus, the purpose of this work is seeking synthesis procedure to obtain composites materials based on MOFs and their researching in the adsorption of organic compounds.

The composite based on HKUST and polyethylene terephthalate (PET) fabric was obtained by in situ formation of MOF on the PET surface. Fragments of PET fabric were pre-impregnated by $Cu(NO_3)_2 \cdot 3H_2O$ aquas solution, dried, mixed with ethanol-water solution of trimesic acid and subjected by hydrothermal treatment. The formation of MOF on the PET surface was proven with methods of low temperature nitrogen adsorption-desorption, XRD and IR-analysis. The specific surface area of the composite was 256 m^2/g and MOFs concentration in the composite was ~17%.

References

1. Cai G., Yan P., Zhang L., Zhou H.C., Jiang H.L., Chem. Rev., 2021, 121, 12278–12326.
2. Feng L., Wang K.Y., Lv X.L., Yan T.H., Zhou H.C., Nat. Sci. Rev., 2020, 7, 1743–1758.
3. Torres-Cortés S.A., Velasquez M., Pérez L.D., Sierra C.A., J. Pol. Res., 2022, 29, 427.

The influence of nickel content in the process of carbon dioxide methanation on glass-fiber catalysts with a secondary layer

Ia.A. Mikhailov [1], A.V. Matigorov[1], S.A. Lopatin[1,2], A.N. Zagoruiko[1,2], A.V. Elyshev[1]

[1]University of Tyumen, Tyumen, Russia
[2]Boreskov Institute of Catalysis of the Siberian Branch of the RAS, Novosibirsk, Russia

y.a.mikhajlov@utmn.ru

Methanation of carbon dioxide is a promising method for reusing CO_2 [1]. One of the key tasks of methanation reactions is the development of an active, selective, and stable catalyst for efficient carbon dioxide conversion. Although Ru and Pt-based catalysts have high activity and stability, their high-cost limits industrial application. Nickel catalysts, in turn, are of greater interest due to their satisfactory activity and low production cost [2, 3].

The particle size and textural properties of the catalyst play a significant role in CO_2 methanation. Nickel is typically deposited on porous carriers such as SiO_2 to improve dispersion [4]. However, the low-temperature activity of Ni/SiO_2 for CO_2 methanation is often small even at high Ni content. Therefore, nickel loading is an important parameter for determining the number of available active centers [5, 6].

Another promising carrier material with high thermal stability, mechanical strength, and improved hydrodynamic properties is glass-fiber. It allows for the development of new types of structured catalytic layers and reactors with high mass transfer efficiency and low pressure drop [7].

In this work, the influence of Ni loading on catalysts obtained by pulse surface thermosynthesis (PST) on glass-fiber with a secondary SiO_2 layer is investigated. The results are compared with the industrial catalyst $16\%Ni/Al_2O_3$.

A secondary SiO_2 carrier layer was preliminarily applied to the original glass-fiber to develop the surface, onto which the precursor – hexahydrate nickel nitrate – was impregnated. The precursor composition additionally included a fuel additive (ethylenediamine). The amount of precursor was calculated to obtain glass-fiber catalysts samples with a Ni concentration of 10 wt.% (S1) and 5 wt.% (S2). The samples were prepared by the PST method, in which the catalyst was heated to 600°C in 10 s. The industrial catalyst $16\%Ni/Al_2O_3$, designated (P), was used as a sample for comparison. The catalysts were reduced in a hydrogen stream at a temperature of 300°C for 2 h.

X-ray phase analysis was carried out for all samples and the crystallite size was calculated in the TOPAS 4.2 software. During the reduction, Ni crystallites of the following sizes were obtained: 30 nm (S1), 25 nm (S2), and 40 nm (P).

The catalytic efficiency of CO_2 methanation was determined in a vertical flow reactor with a fixed bed. After the catalyst was reduced, a mixture of 80 vol.% H_2 and 20 vol.% CO_2 without dilution was introduced into the catalyst bed through a mass flow controller at a rate of 50 ml/min of gas mixture (40 ml/min H_2 and 10 ml/min CO_2). Tests of catalytic activity for CO_2 methanation were conducted on various catalysts within a specified temperature range (250–400°C) and at a pressure of 1 bar.

For accurate comparison of the catalytic properties of different samples, specific activity indicators per unit mass of the catalyst k_m (equation 1), per unit mass of nickel k_{mNi} (equation 2), and per unit volume of the catalytic layer k_V (equation 3) were used in the form of the value of the first-order reaction rate constant for CO_2.

$$k_m = \frac{Q}{m_{cat}} \ln\left(\frac{CO_2,in}{CO_2,out}\right), (\mathrm{norm.m^3g^{-1}s^{-1}}) \tag{1}$$

$$k_{mNi} = \frac{Q}{m_{Ni}} \ln\left(\frac{CO_2,in}{CO_2,out}\right), (\mathrm{norm.m^3g^{-1}s^{-1}}) \tag{2}$$

$$k_V = \frac{Q}{V} \ln\left(\frac{CO_2,in}{CO_2,out}\right), (\mathrm{s^{-1}}) \tag{3}$$

Q is gas flow rate, (norm. m^3/s), m_{cat} is catalyst mass (g), m_{Ni} is active component mass (g), V is cartridge volume, (m^3).

The following results were obtained from the catalytic test: 1) CO_2 conversion of samples S1, S2 and P was 41%, 43% and 63% respectively; 2) CH_4 yield was 41.0% (S1), 43.0% (S2) and 60.5% (P); 3) activity per unit mass of the catalyst was 17.5 (S1), 20.8 (S2) and 18.9 (P); 4) activity per unit mass of nickel was 20.4 (S1), 39.6 (S2) and 11.7 (P); 5) activity per unit volume of the catalytic layer was 15.6 (S1), 17.2 (S2) and 15.5 (P).

Despite the lower nickel content, glass-fiber catalysts (S1 and S2) demonstrate significantly higher catalyst activity per unit mass of the active component (S2 (39.6); S1 (20.4)) compared to the industrial catalyst P (11.7). In addition, with a lower nickel content, particles of the active component can be more evenly distributed over the carrier surface, which promotes better contact of reagents with active centers.

All this indicates that the catalyst with a 5% nickel content on glass-fiber has the highest efficiency of using the active component.

The research was carried out with the financial support of the Government of the Tyumen Region under the project of the West Siberian Interregional Scientific and Educational Center № 89-DON (3), as well as with the support of the Ministry of Science and Higher Education of the Russian Federation within the framework of the state assignment for the Boreskov Institute of Catalysis (project FWUR-2024-0037).

The synthesis and characterization of fibrous glass catalyst samples were funded by the Russian Science Foundation grant № 22-73-10015, https://rscf.ru/project/22-73-10015/.

References

1. Wilberforce T., Olabi A.G., Sayed E.T. Sci. Total Environ., 2021, 761, 143203.
2. Chuanfei Liang, Tao Wei, Hui Wang. J. Energy Inst., 2020, 93, 723–738.
3. Singh S.A., Mukherjee S., Madras G. Mol. Catal., 2019, 466, 167–180.
4. Zhang Y., Chen Y., Liu Q. Int. J. Hydrogen Energ., 2021, 46, 32003–32016.
5. Riani P. Int. J. Hydrogen Energ., 2023, 48, 24976–24995.
6. Gac W. Microporous Mesoporous Mater., 2018, 272, 79–91.
7. Zagoruiko A.N., Lopatin S.A. Structured Glass-Fiber Catalysts. Francis & Taylor group, CRC Press, 2019.

Design of catalysts based on CeO_2-Fe_2O_3@SBA-15 for deep oxidation of volatile organic compounds

N.N. Mikheeva, G.V. Mamontov

Tomsk State University, Tomsk, Russia

natltiv93@yandex.ru

With the growth and development of industry, the problem of air pollution by volatile organic compounds (VOCs) is becoming more and more urgent [1]. The oxidation of VOCs into CO_2 and water is one of the most effective methods of controlling VOCs emissions into the air. Systems based on iron and ceria oxides are of great interest as catalysts for the oxidation of VOCs that do not contain noble metals [2, 3]. However, these systems have a few disadvantages, such as relatively low porosity and low thermal stability, which limits their practical application. To solve this problem, an inert support is used, for example, SiO_2, which provides a developed porous structure.

The purpose of this work was to develop toluene oxidation catalysts based on CeO_2-Fe_2O_3@SBA-15. The hybrid Pluronic@SBA-15 system was used as a precursor to the primary support, which is an intermediate product of the synthesis of SBA-15 containing the Pluronic P123 triblock-copolymer in a porous space [4]. Ceria and iron oxides were introduced by moisture impregnation method with using $Ce(NO_3)_3$ and $Fe(NO_3)_3$ as precursors.

The textural characteristics of the synthesized samples were studied by low-temperature nitrogen adsorption. According to the data obtained, all samples have a similar porous structure: a narrow pore size distribution (5-7 nm) and a high specific surface area (750-810 m^2/g). The data obtained indicate the distribution of iron and ceria oxides in the form of highly dispersed particles evenly distributed in the porous space of SBA-15. This distribution was achieved by using the hybrid material Pluronic@SBA-15, in which the block copolymer Pluronic P123 inside the pores of SBA-15 stabilizes the precursors of oxides and promotes the formation of very small oxide particles [4]. The XRD method failed to detect Ce- and Fe-containing phases, which confirms their stabilization in a highly dispersed state (less than 3 nm in size).

According to the data obtained by the TPR H_2 method, the CeO_2@SBA-15 sample is characterized by the presence of a peak in hydrogen absorption in the temperature range of 300-650 °C, related to the reduction of surface centers of Ce^{4+} to Ce^{3+}. The absence of a high-temperature peak in the 700-900°C region, related to the reduction of the bulk of CeO_2 particles, confirms the formation of highly dispersed CeO_2 particles. An increase in the addition of iron oxide leads to a shift in the peak of hydrogen consumption to a lower temperature region, as well as to an increase in the amount of consumed hydrogen, which may indicate the interaction of iron and cerium oxides and have a positive effect on the catalytic properties of the obtained systems in oxidative processes.

Thus, a series of CeO_2-Fe_2O_3@SBA-15 with dispersed uniformly distributed particles CeO_2 and Fe_2O_3 was obtained. The dispersion of particles, as well as the interaction of CeO_2 and Fe_2O_3, affects the redox properties of systems and can affect the catalytic properties in the oxidation reaction of VOCs.

This work was supported by the Russian Science Foundation, Grant № 23-73-10152.

References

1. Torregrosa-Rivero V., Sánchez-Adsuar M. S., Illán-Gómez M. J., Nanomaterials, 2022, 12 (2), 219.
2. Rodriguez J.A., Grinter D.C., Liu Z., et. al., Chemical Society Reviews, 2017, 46, 1824.
3. Zhou Y., et al., Chemical Engineering Journal, 2023, 475, 146198.
4. Taratayko A., et al., Catalysis Today, 2021, 375, 576–584.

Titanium-modified Zr-UiO-66 metal-organic framework as a catalyst for cascade conversion of dihydroxyacetone to lactic acid

S.N. Nikulaichev, V.V. Torbina, O.V. Vodyankina

Tomsk State University, Tomsk, Russia

nikulaichev.s.n@gmail.com

Processes to obtain valuable products such as bifunctional organic acids from biomass processing are a relevant area of catalytic chemistry today. Glycerol is a by-product of biodiesel production and represents an available feedstock for manufacturing of more expensive products such as dihydroxyacetone (DHA). DHA can be isomerized to value-added product, i.e., lactic acid [1], and the process is of interest due to the extensive application of the product in food, pharmaceutical and cosmetic industries as well as for the production of biodegradable polymers. However, the process is a rather complex cascade reaction proceeding through a multistep route including oxidation and isomerization steps [2]. The first step involves oxidation of the primary or secondary hydroxyl groups to form glyceraldehyde or DHA, respectively. In the presence of Lewis acid catalyst, glyceraldehyde is rapidly converted to the thermodynamically stable DHA. The Lewis acid sites promote the dehydration reaction and rearrangement of intermediates to efficiently produce lactic acid. Thus, the corresponding active sites play a key role in the selective glycerol conversion to lactic acid.

The aim of this work is to develop approaches to control Lewis acid sites by partial substitution of Zr atoms for Ti ones in the structure of metal-organic framework UiO-66 to improve the conversion efficiency of DHA to lactic acid.

The synthesis of Ti-UiO-66 was carried out under solvothermal conditions in a Teflon-coated stainless steel autoclave according to the procedure similar to that described in Ref. [3] with replacement of the required amount of $Zr(NO_3)_2{\cdot}2H_2O$ with $C_{10}H_{10}TiCl_2$. The obtained materials were characterized by XRD, low-temperature N_2 adsorption, Raman and IR spectroscopies, and scanning electron microscopy. Catalytic experiments were carried out in a thermostated Parr reactor. 30 mL of aqueous solution of DHA (0.3 M) and 200 mg of catalyst were incubated at 100 °C at a vigorous stirring for 4 h. After removal of the catalyst, the reaction mixture was analyzed by HPLC.

According to the results of SEM and XRF analysis, in all samples the Zr/Ti molar ratios are close to the theoretical ones (5, 10, 33 mol. %), and metals are distributed in most of the particles homogeneously. The crystal structure of the Ti-bearing samples also corresponds to the UiO-66 phase. No impurities of crystalline phases of titania were found even at high titanium loading. The Ti introduction by the used method results in a slight decrease in the specific surface area and porosity of UiO-66. At the same time, the Ti introduction into Zr-UiO-66 results in a significant increase in selectivity towards lactic acid.

The report will also discuss the influence of the synthesis conditions of the Ti-modified MOFs as well as new approaches to their application to environmental challenges and photosynthesis.

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

References

1. Wang K., et al., Journal of Energy Chemistry, 2024, 91, 542–578.
2. Rahaman M.S., et al., ChemCatChem, 2022, 14, 4, e202101756.
3. Torbina V.V., et al., Catal. Today, 2019, 333, 47.

A nanostructured ceramic involving intense luminescence for fast photodissociation of gas molecules

N. Ouarab[1], N. Redjdal[1], L. Benharrat[1], S. Mezghiche[1], A. Cheriet[1], Aboumustapha[2],
Y. Si-Ahmed[1], S. Bouachma[1], Z. Charfi[1], K. Derkaoui[1]

[1]Research Center in Semiconductors Technology for Energetic-(CRTSE), Algeria
[2]Scientific and Technical Research Center in Physico-Chemical Analysis, Bousmail, Tipaza, Algeria

ouarab_nourdine@yahoo.fr, n_ouarab@crtse.dz

Modified clay-based catalysts have been successfully synthesized. It features nanocrystals with high catalytic activity, assisted by the gas-molecule photodissociation technique. The thermoluminescence measurements of our substrates, exposed to the catalyst heat zone, are carried out at 350°C. The result shows a sharp peak at 335 nm, which in turn causes highly intense range-gap photoluminescence from 510 nm to 376 nm due to the impregnation of activated nanoparticles of $AlPO_4$. Therefore, the obtained wavelength energy enables efficient dissociation of CO, NO_x, and C-C molecules. The catalyst helps, with the CO oxidation, the CO_2 conversion to the methane, reaching a conversion rate of 100%, while CH_4 selectivity reaches 98%. Our results attest to the added performance of our catalyst based on a new dynamic model. So, photo-luminescence and small pores are two key parameters enabling the best reactivity with studied gases and the development of new low-cost automobile catalysts.

The analysis of the catalyst reveals that the resulting clay has a stoichiometric equilibrium between alumina (45%) and silica (51%). X-ray diffraction results, in case of samples submitted to impregnation and calcination treatment at 1000 °C, show peaks of crystallized kaolinite. It has a purity order of up to 65%, so, the other peaks are associated with alumina Al_2O_3 revealing the existence of crystallographic phases of artificial zeolite and dickite. In the analyses of XPS and ATR-FT-IR spectroscopy, the results show, in particular, the appearance of wave number at ~ 914 cm^{-1} assigned to Al-Al-OH stretching, which is very significant. The characteristic peak at 675 cm^{-1} attributed to Al-O-Si deformation also confirms the previous finding, as well as the appearance of weak Si-O stretching of quartz at 750 cm^{-1}. Therefore, the results of XPS analysis reveal binding energies of octahedral coordination of Al-2p at (74.5±0.2) eV and (102.7 ±0.2) eV of Si-2p, very particularly comes from kaolinite. Our results are consistent and disclose the successful synthesis of kaolinite in elaborate experimental conditions.

We significantly analyzed exhaust gases from a four-wheeled test vehicle, without catalytic converter, using the GC/FID chromatograph (HP /Agilent 6890 system) to determine the chemical composition of these gases. Real operating conditions were recreated in the laboratory to test our catalytic converter. The result shows a catalytic performance under specific condition of temperature revealing the removing all of volatile substances.

Keywords: Phyllosilicates clay materials, ceramics based-catalyst, nano-structures, acids impregnation process, CO_2 conversion, and fuel.

This work was financially supported by the National Research Fund DGRSDT/MESRS (Algeria).

References

1. Zvonareva S.V., Pankov V.A., Churkin V.Y., Chesnokov K.Yu., Chukin A.V., Abramov A.V., Physics Research B, 2020, 471, 53–58.
2. Xu L., Xiu Y., Liu F., Liang Y., Wang S., Molecules, 2020, 25, 3653, 1–23.
3. Wu J., Yadav R. M., Liu M., Sharma P.P., Tiwary C.S, Ma L., Zou X., Zhou X.D., Yakobson B.I., Lou J. Jayan P.M., ACS Nano, 2015, 9, 5364–5371.
4. Uttamaprakrom W., Reubroycharoen P., Charoensiritanasin P., Tatiyapantarak J., Srifa A., Koo-Amornpattana W., Chaiwat W., Sakdaronnarong C., Sudoh M., Watanabe R., Fukuhara C., Ratchahat S., Enviro J., Chem. Engin, 2021, 9, 106150 (1–12).
5. Zhao S., Guo S., Zhu C., Gao J., Li H., Huang H., Liu Y., Kang Z., RSC Adv, 2017, 7, 1376–1381.
6. Zakaria S.N.A., Hollingsworth N., Islam H.U., Roffey A., Santos-Carballal D., Roldan A., Bras W., Sankar G., Hogarth G., Holt K.B., de Leeuw N.H., ACS Appl. Mater. Interfaces, 2018, 10 32078−32085.
7. Nandanwar C.M., Yerojwar R.M., Kokode N.S., Yerpude A.N., Dhoble S.J., Indian J Phys, 2024, 98, 1083–1093.

8. Trukhin A.N., Shmits K., Jansons J.L., Boatner L.A., J. Phys.: Condens. Matter, 2013, 25, 385502 (1–6).
9. Ovhal D.A., Chopra V., Dhoble N.S., Dhoble S.J., Journal of Molecular Structure, 2021, 1225 129135 (1−10).

Designing ZrO_2-MnO_x-based catalysts for CO oxidation

Ya.E. Salnikov, N.N. Mikheeva, G.V. Mamontov, M.V. Grabchenko, M.A. Salaev

Tomsk State University, Tomsk, Russia

yaroslaw.salnikov@yandex.ru

Due to the constantly increasing number of vehicles on the roads, there has recently been an increase in environmental pollution from exhaust gases [1]. Exhaust gases contain dangerous substances (CO, nitrogen oxides, hydrocarbons, aldehydes, etc.) and pose a danger to the environment and human [2]. To solve this problem, it is important to develop new catalysts for the total oxidation of combustion products. Manganese oxides feature good catalytic activity, but low thermal stability as well as extremely low specific surface area. The thermal stability and specific surface area can be increased by adding ZrO_2 to the composition. The aim of this work was to synthesize catalysts based on ZrO_2 and MnO_x by hydrothermal synthesis [3] with cetyltrimethylammonium bromide (CTAB) as a structure-forming additive.

The obtained samples were studied using a number of physical-chemical methods, including low-temperature nitrogen adsorption method, XRD and TPR methods, and tested in the CO oxidation reaction.

The low-temperature nitrogen adsorption results show that the resulting ZrO_2-MnO_x samples feature a mesoporous structure and a relatively high specific surface areas (100-120 m^2/g), while individual ZrO_2 and MnO_x are characterized by low specific surface areas of 39 and 7 m^2/g, respectively. As the amount of added MnO_x increases, both specific surface area and pore volume of the catalysts increase.

The XRD data show that in mixed oxide systems there are no reflections related to manganese oxide, except for the samples $Mn_{0.33}Zr_{0.67}O_2$ and $Mn_{0.2}Zr_{0.8}O_2$ exhibiting weak reflections of Mn_2O_3, which indicates that it is either in a highly dispersed state or is included into the ZrO_2 structure. This indirectly confirms that uncharacteristic cubic ZrO_2 phase is predominant in the mixed oxide samples. The TPR data, i.e., the shift of the hydrogen consumption peaks towards lower temperatures with a decrease in the Mn_2O_3 content, confirm that the oxides actually interact, since the individual ZrO_2 and MnO_x oxides are reduced at higher temperatures.

When assessing the catalytic ability in CO oxidation, it was found that the most active catalyst is $Mn_{0.2}Zr_{0.8}O_2$ ($T_{50\%}$=156°C, $T_{98\%}$=300 °C).

Thus, the catalysts based on ZrO_2 and MnO_x were obtained. XRD and TPR data confirm the contact between manganese and zirconium oxide particles, which can have a positive effect on the catalytic properties of the obtained systems. The obtained data are promising for development of new generations of catalysts for environmental applications.

This work was supported by the Russian Science Foundation, Grant № 23-73-00109.

References

1. Denisov V.I., Rogalev V.A., Problems of greening road transport. − St. Petersburg: MAPEB, 2005.
2. Grabchenko M.V., et al., Chemical Engineering Science, 2024, 285, 119593.
3. Pan C., Zhang D., Shi L. Journal of solid-state chemistry, 2008, 181 (6), 1298–1306.

Hydroisomerization of high C_{16}+ paraffins on granulated Pt-containing molecular sites SAPO-11 and ZSM-23

V.I. Zaripov[1], D.V. Serebrennikov[1], R.E. Yakovenko[2], I.N. Zubkov[2], O.S. Travkina[1],
A.I. Malunov[1], A.R. Zabirov[1], G.T. Bagautdinova[3], A.N. Khazipova[1], B.I. Kutepov[1], M.R. Agliullin[1]

[1]Institute Petrochemistry and Catalysis UFRC RAS, Ufa, Russia
[2]Platov South-Russian State Polytechnic University (NPI), Novocherkassk, Russia
[3]Ufa State Petroleum Technical University , Ufa, Russia

zaripowalerii@mail.ru

Over the past 20 years, winter diesel fuel production technologies have been developed through the development and implementation of the isodewaxing process. This process has significantly increased the yield of the final product. The isodewaxing process involves the selective hydroisomerization of higher n-paraffins in the C16+ diesel fraction into isoparaffins using bifunctional catalysts with Pt deposited on acid molecular sieves. The molecular sieves used in this process have a one-dimensional channel porous structure with an average pore size of ~5 Å. Materials such as ZSM-23 aluminosilicates and SAPO-11 silicoaluminophosphates are particularly effective in this regard.

It should be noted that in industrial catalytic isodewaxing processes, molecular sieves are used in the form of granules. These granules are created by combining powdered zeolite with binde materials, such as aluminum monohydroxide, followed by drying and calcining at 500-650 °C. During the process of creating the granules, there may be a partial blockage of the pores in the zeolite crystals by the particles of the binding material, which can lead to a reduction in the availability of catalytic active sites and may also cause increased adverse reactions such as hydrocracking. Despite the numerous publications on the study of the catalytic properties of these molecular sieves for the hydroisomerization of higher paraffins with carbon C16+, there is little information available in the literature on the effect of binders and their content on the catalytic performance of the granulated materials based on zeolites.

The paper investigates the catalytic properties of platinum-containing (0.5% by weight) molecular sieves, SAPO-11, ZSM-23, and ZSM-5, with different binder contents (from 20% to 60% by weight), based on pseudoboehmite, in the hydroisomerization of n-hexadecane and a diesel fraction. These molecular sieves were also studied without binding materials, which were obtained by a method described in [3]. The samples of SAPO-11, ZSM-23, and ZSM-5 have specific surface areas of S_{BET} ranging from 150 to 292 m^2/g, micropore volumes of V_{micro} ranging from 0.05 to 0.08 cm^3/g, mesopore volumes of V_{meso} ranging from 0.1 to 0.2 cm^3/g, and total acidities of NH_3 ranging from 150 to 490 mmol/g. The hydroisomerization process of n-hexadecane and the diesel fraction took place in a flow reactor under conditions of 3 MPa, 250–340°C, and 1.5–2.0 h^{-1}.

It has been demonstrated that granular Pt-containing molecular sieves, such as SAPO-11 and ZSM-23, provide a higher yield of isoparaffins compared to ZSM-5 due to their one-dimensional channel structure. The fusion of these materials with activity systems such as SAPO-11, ZSM-23 and ZSM-5 has resulted in a significant improvement in efficiency, ranging from 20% to 60%, which is a crucial aspect of the process. Samples of granular molecular sieves with and without binders have shown that those without binders provide higher activity and selectivity. It has been found that SAPO-11 granules without binders are the most effective catalysts for hydroisomerizing higher n-paraffins, such as C16. This allows for an isomer yield of more than 87%, as well as producing winter diesel fuel with a freezing point of -50°C and an isomerization yield of over 99%.

This work was supported by the state assignment of the UFRS IPC RAS (№FMRS-2024-0012 "Molecular sieve bifunctional catalytic systems for the production of winter and arctic diesel fuels").

References

1. Akhmedov V.M., Al-Khowaiter S.H., Catalysis Reviews, 2007, 49 (1), 33–139.
2. Ertl G., Knözinger H., Schüth F., Weitkamp, J. Handbook of Heterogeneous Catalysis, 2008.
3. Agliullin M.R., Kutepov B.I., Grigoreva N.G., Pavlova I.N., RU Patent 2 776 916 C2, 2022 .

SECTION 2

PROMISING CATALYTIC PROCESSES

Modification of g-C_3N_4 and TiO_2 with Ti_3C_2X MXenes for photocatalytic CO_2 reduction

R.F. Alekseev[1,2], A.Yu. Kurenkova[1], K.O. Potapenko[1], D.B. Vasilchenko[3], E.A. Kozlova[1]

[1]Boreskov Institute of Catalysis, Novosibirsk, Russia
[2]Novosibirsk State University, Novosibirsk, Russia
[3]Nikolaev Institute of Inorganic Chemistry, Novosibirsk, Russia

r.alekseev@g.nsu.ru

Currently, the problem of growing greenhouse gas emissions is becoming increasingly important, and therefore their utilization is the topic of many studies. Special attention is paid to carbon dioxide utilization. One of the most promising approaches to this process is photocatalytic CO_2 reduction [1]. In addition to the fact that this technology allows decreasing the amount of carbon dioxide in the atmosphere, CO_2 reduction products, such as methane, methanol, formic acid, can be used for the production of synthetic fuels and in other types of chemical industries [2]. It is also worth noting that the photocatalytic process of CO_2 reduction occurs at ambient conditions with the use of only renewable resources: light and water.

The aim of this work is to investigate the effect of modification of TiO_2 and g-C_3N_4 photocatalysts with Ti_3C_2X MXenes in the reaction of photocatalytic reduction of CO_2 under LED irradiation with a wavelength of 397 nm.

Commercial “Evonik P25” was used as a source of TiO_2, and g-C_3N_4 was prepared by calcination of a mixture of melamine and urea (1:3 ratio) at 525°C for 1 hour. To obtain MXenes the MAX phase Ti_3AlC_2 was etched for 3 days in a solution containing LiF and HCl. After this, the sediment was washed until pH=6 and centrifuged, after which the suspension above the sediment was taken, which was then mixed with TiO_2 or g-C_3N_4 and dried in a vacuum oven at 60°C for 12 hours to obtain the respective modified samples (Ti_3C_2X/TiO_2 and Ti_3C_2X/g-C_3N_4). The synthesized photocatalysts were characterized by XRD, XPS, HR TEM, and UV-vis diffuse reflectance spectroscopy.

The photocatalytic reduction of CO_2 was carried out in a batch reactor (170 ml) with a quartz window. Before the reaction the photocatalyst was irradiated with ultraviolet light (365 nm) for 15 minutes to remove organic contaminants from the surface of the photocatalyst and then placed in a reactor containing 1 ml of ultrapure water. Next, the reactor was purged with argon for 20 minutes to remove oxygen, and then with CO_2 (99.995%) for another 20 minutes, after which the LED was turned on (397 nm, 60 mW/cm^2). Kinetic experiment was carried out for 5 hours. Every hour gas probe was taken with a gas syringe (500 μl) and analyzed with a gas chromatograph.

The main product of CO_2 reduction process over composite photocatalysts was CH_4, also CO was formed. To compare activities of photocatalysts the total electron consumption rate was calculated ($W_e = 8\cdot W(CH_4)+2\cdot W(CO)$). Thus, the highest activity was achieved for 5% Ti_3C_2X/TiO_2 (20 μmol g^{-1} h^{-1}), which was 2.8 times more active than the unmodified TiO_2 (7.1 μmol g^{-1} h^{-1}). The increase in activity was attributed to the increase of visible light absorbance (as proved by DRS results) and to the formation of electron traps due to the Schottky junction, which increases the efficiency of light utilization by decreasing the recombination rate of photogenerated electron-hole pairs. In the case of g-C_3N_4, higher Ti_3C_2X concentration leads to higher activity with the electron consumption rate of 8.6 μmol g^{-1} h^{-1} for 10% Ti_3C_2X/g-C_3N_4 (vs. 5.8 μmol g^{-1} h^{-1} for the unmodified g-C_3N_4). To explain this, it is shown by DRIFTS in-situ that g-C_3N_4 is barely able to adsorb CO_2 molecules on its own, which is why a higher content of Ti_3C_2X is required.

This work was supported by the Russian Science Foundation, Grant № 24-13-00416.

References

1. Alekseev R.F., Saraev A.A., Kurenkova A.Yu., Kozlova E.A., Russ. Chem. Rev., 2024, 93, RCR5124.
2. Saraev A.A., Kurenkova A.Yu., Gerasimov E.Yu., Kozlova E.A., Nanomater., 2022, 12, 1584.

High-performance Ni/Al_2O_3-(Zr+Ce)O_2 catalysts for syngas production via ethanol dry reforming

Yu.A. Fionov, K.S. Khlusova, S.G. Chuklina, S.M. Semenova, S.V. Khaibullin, A.I. Zhukova

RUDN University, Moscow, Russia

fionovyuri@gmail.com

The concentration of carbon dioxide in the atmosphere has been progressively increasing for decades, which makes it extremely important to develop effective methods of CO_2 utilization. A sufficient amount of CO_2 can be converted using carbon dioxide conversion processes. In addition to the dry reforming of methane, another promising alternative for CO_2 conversion is dry reforming of bio-alcohols, which occur at lower temperatures. The process of ethanol dry reforming (EDR) is considered as one of the environmentally friendly methods of reducing greenhouse gas emissions while increasing the production of value-added syngas (H_2 + CO) [1]. It was previously established that nickel catalysts with an aluminum-ytterbium stabilized complex oxide carrier showed high activity and stability in the EDR reaction [2].

In this paper, the effect of the composition of an alumina-zirconia catalysts (Ni/xAl_2O_3-(100-x)-(0.88Zr+0.12Ce)O_2 with x=5, 20, 50, 75 mol.% Al_2O_3 (Ni/xACZ) on activity and stability in EDR was studied. The genesis of Ni^0 nanoparticles under the reaction conditions (650ºC, 7 hours on stream) (CO_2:EtOH=1.8:1) was carried out using UV-Vis absorption spectroscopy and Raman spectroscopy, X-ray phase analysis (XRD), ferromagnetic resonance (FMR), high-resolution transmission electron microscopy (HRTEM) and H_2-TPR. The ratio CO_2:EtOH=1.8:1 was used to reduce carbon accumulation and increase the stability of the catalyst during the EDR reaction. The Ni^0 particle stabilization strategy included adjusting the Al/Zr ratio in the carrier composition to fine tune the Ni^0 metal-support interaction (MSI) with the support.

An increase in the Al/Zr ratio (from 5 mol.% up to 75 mol.% of aluminum oxide) led to a decrease in the size of Ni nanoparticles and an increase in the MSI due to the presence of spinel structures in the unreduced catalysts. It was found that the structural properties provide the greatest activity and stability of samples with a high Al content (x=50, 75 mol.%) in the dry reforming of ethanol, due to the increased ability to prevent the deposition of coke on a nickel nanoparticle. Among them, the Ni/50Al_2O_3 catalyst(0.88ZrO_2-0.12CeO_2) demonstrated excellent catalytic activity in the EDR process at 650°C, achieving an optimal synthesis gas ratio of H_2:CO=1:1. Due to the effective adsorption/activation of CO_2 and the strong interaction of the metal with the carrier, the Ni/50ACZ catalyst demonstrated the highest yields for formation of H_2 (42%) and CO (42%) (CO:H_2 ratio=1) at 650°C. Under reforming conditions at 650°C, Ni/50ACZ retains an exceptional conversion of C_2H_5OH and CO_2 (100 and 63%, respectively). It is noteworthy that Ni/50ACZ remained active without deactivation and formation of undesirable by-products such as ethylene, ethane, and acetaldehyde for 7 hours. On the contrary, lower activity and stability in samples with a high Zr content (x = 5.20 mol. %) is due to the large size of nickel particles and the active carbonation of Ni nanoparticles with graphitized carbon. It is shown that the presence of the zirconium phase leads to the formation of large nickel particles (up to 300 nm), and an increase in the content of Al_2O_3 from 5 to 75 mol.% helps to reduce the size of nickel particles from hundreds of nanometers to ~10 nm, respectively. These characteristics highlight its potential for efficient and clean synthesis gas production in an industrial environment.

This work was supported by the Russian Science Foundation, Grant № 23-29-00369.

References

1. Bac S., Keskin S., Avci A.K., Sustain. En. Fuels, 2020, 4, 1029–1047.
2. Zhukova A.I., Fionov Yu.A., Chuklina S.G., Mikhalenko I.I., Fionov A.V., Isaikina O.Ya., Zhukov D.Yu., de Lima A.M., Energy Fuels, 2024, 38, 482–498.

Platinum-modified g-C_3N_4/TiO_2 photocatalysts for H_2 evolution from glucose aqueous solutions

S.N. Kharina, A.Yu. Kurenkova, E.A. Kozlova

Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia

skharina@catalysis.ru

In the context of addressing the energy crisis, there has been a focus on the development of alternative fuels, such as hydrogen. Among numerous methods and techniques, photocatalytic process is considered to be a sustainable one, mainly because it allows us to obtain "green" hydrogen at ambient conditions using renewable sources such as sunlight, water and biomass. A key factor determining the efficiency of the process is a rationally designed photocatalyst. Therefore, desirable photocatalyst properties including absorption of visible light, long-lived electron-hole pairs and surface adsorption properties ought to be considered. The combination of high resistance to photocorrosion and activity under visible light makes composites based on TiO_2 and g-C_3N_4 well applicable for hydrogen evolution from plant biomass components. Additionally, the composite structure of two semiconductors provides an efficient charge separation due to the formation of an II type heterojunction, leading to enhanced hydrogen production rate [1-3].

This work is devoted to the synthesis and investigation of platinum-modified composite photocatalysts based on graphitic carbon nitride and titanium dioxide for H_2 evolution reaction under visible light irradiation. A total of three series of composites, differing in their surface modification techniques, were obtained via mechanical dispersion of 1%Pt/TiO_2 and modified g-C_3N_4. The three g-C_3N_4 surface modification approaches aim to exfoliate and oxidize the surface, and include calcination (g-C_3N_4-500, 500 °C, 1 h) of graphitic carbon nitride, hydrothermal processing (O1-g-C_3N_4, 140 °C, 14 h) and long-term processing of melamine in H_2O_2 (O2-g-C_3N_4, 50 °C, 24 h) followed by calcination at 550 °C. The characterization of the samples has been conducted using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), high-resolution transmission electron microscopy (HR-TEM) and diffuse reflectance electron spectroscopy (DRS).

The photocatalytic activity of the composite photocatalysts was evaluated in aqueous solutions of alpha-D(+)-glucose (C_0=0.1 M) at 20 °C and 1 atm under LED radiation (440 nm). The outcomes of the photocatalytic tests demonstrate that composite photocatalysts exhibit up to a fivefold increase in activity compared to Pt-modified TiO_2. The optimal composition is determined to be 10% g-C_3N_4/1% Pt/TiO_2 for all three series. Among the photocatalysts containing 10 % g-C_3N_4-500, O2-g-C_3N_4 or O1-g-C_3N_4, the photocatalytic activity equals to 713, 627 and 482 $\mu mol \cdot h^{-1} \cdot g_{cat}^{-1}$, respectively. Notwithstanding the observed decreasing trend, H_2O_2 treated photocatalysts exibit high stability and good recyclability during at least 6 hours of operation. The hydrogen evolution reaction from glucose aqueous solutions are proved to fit Langmuir-Hinschelwood kinetic model.

This work was supported by the Russian Science Foundation, Grant 23-73-01161.

References

1. Kocijan M., Vukšić M., Kurtjak M., Ćurković L., Vengust D., Podlogar M., Catalysts, 2022, 12.
2. Mohini R., Lakshminarasimhan N., Mater. Res. Bull., 2016, 76, 370–375.
3. Muñoz-Batista M.J., Kubacka A., Fernández-García M., Catal. Sci. Technol., 2014, 4, 2006–2015.

Laser synthesis and photocatalytic properties of bismuth oxide-halides

V.E. Korepanov, O.A. Reutova, V.A. Svetlichnyi

Tomsk State University, Tomsk, Russia

corepanow.vyacheslaw@yandex.ru

Photocatalytic technologies occupy an important place in solving the problems of sustainable development. Photocatalysis is used for water and air purification, processing biomass into products with high added value, CO2 utilization, hydrogen production and many other applications [1]. The dynamics of development of this area is determined by the creation of new effective, inexpensive and stable photocatalysts and technologies for their production. Among the various photocatalysts, materials based on double oxides with the general structure $Bi_xO_yX_z$ (BiOX), where X is the halogens Cl, Br or I, have recently attracted attention [2]. BiOX photocatalysts and semiconductor composites based on them are promising in the decomposition of organic compounds, inactivation of pathogenic bacteria, reduction of CO_2, etc. [3, 4].

In this work, we first applied laser synthesis to obtain BiOX nanostructures (where X = Br, I) and tested their photocatalytic properties in the decomposition reactions of various organic compounds (Rh B dye, phenol, tetracycline and vancomycin antibiotics), as well as the selective photooxidation of 5-HMF.

The synthesis was carried out in two stages. At the first stage, reactive pulsed laser ablation (R-PLA) of the Bi metal target in aqueous solutions of KBr, KI precursors was carried out under the action of focused radiation of a Nd:YAG laser (λ=1064 nm, τ=7 ns, ν=20 Hz). At the second stage, the obtained colloidal solution was subjected to laser treatment with the same focused radiation to form plasma in the solution (P-LT). The obtained colloidal solutions were settled, the mother liquor was removed, the precipitate was washed with distilled water and dried in the open air at T=60°C. The obtained samples were studied by XRD, SEM and UV-visible spectroscopy.

The obtained bismuth oxide-halides are characterized by high crystallinity and dispersion, the nanoparticles are scales. The main phase in the synthesized systems is the monoclinic phase $Bi_4O_5Br_2$ or $Bi_4O_5I_2$, respectively. The first sample also contains a small amount of β-Bi_2O_3, and the second BiOI. The optical band gap corresponds to the structures determined by the XRD method and is 3.1 and 2.7 eV, respectively.

Both photocatalysts have increased sorption of ionic organic molecules - tetracycline (chloride) and Rh B. At the same time, they also effectively decompose these molecules - the Rh B solution is decolorized in 20 minutes. The resulting photocatalysts effectively decompose the aromatic ring of phenol with virtually no formation of long-wave products, which is typical for many oxide catalysts. BiOX samples show good efficiency and selectivity in the oxidation of HMF. Moreover, deep oxidation to FDCA occurs.

The obtained first results show high efficiency of the synthesized catalysts. In order to further improve their photocatalytic characteristics, better charge separation and expansion of the spectral range, it is planned to create complex composite structures based on the obtained bismuth oxide-halides. It is also planned to test the performance of the obtained catalysts in the reaction of CO_2 photoreduction.

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

References

1. Imam S.S., Adnan R., Kaus N.H.M., Journal of Environmental Chemical Engineering, 2021, 9, 4, 105404.
2. Jimenez-Relinque E., et al., Journal of Photochemistry and Photobiology A: Chemistry, 2024, 452, 115554.
3. Arumugam M., Choi M.Y., Journal of Industrial and Engineering Chemistry, 2020, 81, 237–268.
4. Jin X., et al., Nano Energy, 2019, 64, 103955.

The role of photogenerated active particles in the selective oxidation of 5-hydroxymethylfurfural

M.A. Krainyukova, E.D. Fakhrutdinova, T.S. Kharlamova, V.A. Svetlichnyi

Tomsk State University, Tomsk, Russia

*krainyukovamaria1605@gmail.com

Nowadays biomass is attracting attention as a renewable carbon resource with a wide range of applications. 5-hydroxymethylfurfural (HMF) is of particular interest as a product of lignocellulose processing. The conversion of HMF makes it possible to obtain such products, as 2,5-furandicarboxylic acid (FDC), 2,5-diformylfuran (DFF), and dihydroxymethylfuran (2,5-HMF), which are actively used as precursors in the pharmaceutical and energy industries [1]. HMF can be selectively oxidized using heterogeneous catalytic reactions under heating and high-pressure conditions. Photocatalytic oxidation of HMF is more environmentally friendly and lower cost way of conversion. However, at the moment, this treatment is characterized by relatively low selectivity in the yield of useful products. Thus, the need to increase conversion and selectivity determines the relevance of studying the mechanisms of photocatalytic conversion of HMF.

Photocatalytic oxidation is specified by directly generation by the semiconductor catalyst of electrons (e^-) and holes (h^+), as well as reactive oxygen species subsequently formed – superoxide radical ($•O_2^-$), hydroxyl radical (•OH) and singlet oxygen ($^sO_2$) at interaction of electrons and holes with solvent and oxygen in the reaction medium. To assess the role of active species on conversion and selectivity could be used the “scavenger” method [2]. The purpose of this work is to identify the role of active species in the photocatalytic oxidation of HMF in the presence of highly defective dark TiO_2 using the “scavenger” method.

Highly defective “dark” TiO_2 was prepared via pulsed laser ablation of a titanium metal target (99.9% purity) in distilled water under irradiation of Nd:YAG laser with the following parameters (λ=1064 nm, 7 ns, 20 Hz) [3]. The “scavengers” were used for determination different types of active species are: 1,4-benzoquinone ($•O_2^-$), propanol-2 (•OH), sodium persulfate (e^-), disodium ethyldiaminetetraacetic acid (h^+), as well as 1,4-nitrophenol ($^sO_2$). Photocatalytic conversion of HMF was carried out in a quartz cylinder in the presence of LED with λ = 375 nm (2 W). The initial concentration of HMF is 0.01 M, the loading of TiO_2 photocatalyst is 1 g/l. For better dissolving of the HMF transformation products, sodium carbonate (Na_2CO_3) with a concentration of 0.04 M, was used as an alkaline agent. The concentration of the “scavengers” was 0.005 M. The experiment was carried out under air purging at atmospheric pressure for 8 hours. High performance liquid chromatography was used for sample analysis [4].

When electrons and holes are captured, a significant decrease in selectivity occurs, which is due to a decrease in generation reactive oxygen species. During the work, it was established that when the captured superoxide radical ($•O_2^-$) and singlet oxygen ($^sO_2$) lead to a significant decrease in the conversion of HMF. It can be assumed that these particles are the main driving force of the oxidative process. Moreover, the capturing only singlet oxygen leads to a significant increase in selectivity for the products DFF (13 times) and HMFCA (4.5 times) witch relative to the experiment in the absence of a “scavenger”. The capture of other radical species does not lead to an initial increase in selectivity.

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

References

1. Ojo A.O., Fermentation, 2023, 9, 11, 990.
2. Schneider J.T., et al. PCCP, 2020, 22, 27, 15723.
3. Fakhrutdinova E.D., et. al., Materials, 2020, 13, 9, 2054.
4. Timofeev K.L., et. al., Applied Catalysis A: General, 2023, 656, 119121.

Soot oxidation and SCR-NO_x on $Ag/Ce_{0.5}Mn_{0.5}O_x$/cordierite catalyst

E.S. L’vova[1], T.S. Kharlamova[1], M.V. Grabchenko[1], A.G. Golubovskaya[1],
A.N. Salanov[2], O.V. Vodyankina[1]

[1]Tomsk State University, Tomsk, Russia
[2]Boreskov Institute of Catalysis, Novosibirsk, Russia

lvovaa2014@gmail.com

The number of vehicles powered by diesel engines increases every year. Fuel economy compared to gasoline engines allows producing less carbon oxides but increases the amount of soot and NO_x produced [1]. The use of particulate filters is a promising way to remove soot from exhaust gases. The filter consists of a ceramic support with a honeycomb structure, which can additionally be coated with a catalytic composition responsible for the soot oxidation in the presence of O_2 and/or NO_x [1]. Silver as an active component of the catalyst is competitive to other noble metals (Pt, Pd) in catalytic activity in the process of soot combustion. Cerium and manganese oxides are promising catalyst components because of the increased oxygen mobility in the crystal lattice due to the redox transitions $Mn^{4+}/Mn^{3+}/Mn^{2+}$ and Ce^{4+}/Ce^{3+} [2]. Previous works showed that equimolar CeO_2-MnO_x composite promoted effective soot oxidation [3], SCR-NO_x [4] and high thermal stability due to the formation of a “patchwork” structure.

This work is focused on the influence of the method of deposition of the $Ag/Ce_{0.5}Mn_{0.5}O_x$ catalyst on the cordierite ceramic support on the composition, structure, morphology and distribution of components over the cordierite surface as well as the catalytic activity of $Ag/Ce_{1-x}Mn_xO_{2-d}$/cordierite systems in the soot oxidation with oxygen and in the presence of NO_x.

The deposition of the catalytically active $Ag/Ce_{0.5}Mn_{0.5}O_x$ composition onto the cordierite support was carried out using the suspension impregnation method, impregnation with aqueous solutions of salts or the sol-gel method for deposition of $Ce_{0.5}Mn_{0.5}O_x$ followed by the Ag deposition by impregnation from an aqueous solution of $[Ag(NH_3)_2]NO_3$. The activity of the $Ag/Ce_{0.5}Mn_{0.5}O_x$/cordierite samples in soot combustion process was studied in a flow reactor in the TPR mode with the MS analysis of evolving gases. The catalytic activity in soot oxidation in the presence of NO_x was studied in a flow catalytic unit equipped with electrochemical detection of CO/CO_2 and IR detection of NO_x.

When using the sol-gel method, it was possible to achieve the specified composition, structure and relatively uniform distribution of $Ce_{0.5}Mn_{0.5}O_x$ over the cordierite surface, which was confirmed by the results of SEM, EDX, Raman spectroscopy, and TEM. The results of the catalytic experiment showed that the presence of NO in the reaction mixture inhibited the soot oxidation process, which was associated with the competitive soot oxidation and NO adsorption at the same active sites of the catalyst. The CO addition to the $NO+O_2$ reaction mixture promoted the effective implementation of the coupled processes of soot oxidation and selective NO reduction to N_2.

Thus, the sol-gel method allows preparing the $Ag/Ce_{0.5}Mn_{0.5}O_x$ catalytic material with the given composition and microstructure to uniformly coat the cordierite surface ensuring efficient soot oxidation under loose contact conditions. The use of the cordierite-supported systems results in the selective soot oxidation to CO_2, while the bulk experiment leads to the formation of both CO and CO_2.

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

References

1. Lee E.J., Kim M.J., Choung J.W., Kim C.H., Lee K.Y., Appl. Catal. A, 2021, 627, 118396.
2. Liberman E.Yu., Kleusov B.S., Naumkin A.V., Zagainov I.V., Konkova T.V., Simakina E.A., Izotova A.O., Adv. Mater., 2020, 9, 75–87.
3. Grabchenko M.V., Kharlamova T.S., L’vova E.S., Bugrova T.A., Vasilchenko D.B., Vodyankina O.V., Russ. Phys. J., 2023, 66, 105.
4. Greca E.L., Kharlamova T.S., Grabchenko M.V., Consentino L., Savenko D.Y., Pantaleo G., Kibis L.S., Stonkus O.A., Vodyankina O.V., Liotta L.F., Nanomater., 2023, 13, 873.

Synthesis and investigation of Cu-containing deep oxidation catalysts for a fluidized bed based on spherical γ-Al_2O_3 strengthened with magnesium

A.P. Lyulyukin[1,2], Y.V. Dubinin[1], V.A. Yakovlev[1]

[1]*Boreskov Institute of Catalysis, Novosibirsk, Russia*
[2]*Novosibirsk State University, Novosibirsk, Russia*

lyulyukin2@catalysis.ru

The main goal of Russia's energy strategy is the optimal use of natural resources to ensure high efficiency in the energy sector [1]. In addition to traditional sources of energy (fossil fuels), there is a particular interest in the modern world in renewable energy sources, substandard fuels and waste for use as energy carriers. However, existing traditional methods have several significant disadvantages, making it economically and environmentally impractical. Therefore, the development of new technologies capable of addressing this issue is a particularly relevant task.

The most common method of processing fuels and waste is incineration. However, traditional incineration (flaring, layered) does not allow for the efficient processing of most substandard fuels and waste. Key factors limiting their use include high levels of pollutants (CO, NO_x, SO_2, dioxins) in the exhaust gases, high process temperatures (1200-1600 ºC), low combustion efficiency, large size and metal intensity of structures, and high demands on structural materials [2].

A promising method that combines high combustion performance of waste and substandard fuels with high environmental safety is the technology of catalytic fluidized bed combustion. It is based on the use of a fluidized bed of catalyst particles mixed with inert material, allowing for the simultaneous release and transfer of heat in a unified pseudo-liquid layer at a specific air-to-fuel ratio close to stoichiometric [3].

To achieve high combustion efficiency in a fluidized bed, a high-strength and active catalyst is primarily required. Currently used catalytic systems have low mechanical strength, preventing the catalyst from working for an extended period in fluidized bed conditions, and often contain carcinogenic chromium. This work is dedicated to the synthesis and investigation of a non-chromium, copper-containing catalyst based on strengthened magnesium spherical granules of aluminum oxide. To achieve this goal, experiments were conducted to optimize the preparation conditions, as well as to study the physico-chemical properties of the resulting copper magnesium catalyst. In the study of mechanical, structural and textural characteristics, the following analysis methods were used: low-temperature nitrogen adsorption, abrasion, crushing, X-ray phase analysis (XRF), scanning electron microscopy (SEM), determination of the 50% CO conversion temperature, elemental analysis.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the governmental assignment for Boreskov Institute of Catalysis (project FWUR-2024-0038).

References

1. The Russian Government, Energy Strategy of Russia for the period up to 2030, 2009, 13.
2. Simonov A.D., Fedorov I.A., Dubinin Y.V., Yazikov N.A., Yakovlev V.A., Parmon V.N., Catalysis in Industry, 2013, 5, 42–49.
3. Simonov A.D., Yazykov N.A., Yakovlev V.A., Parmon V.N., Patent RU 256978C1, 2015.

Modified iron-based catalysts for producing valuable chemical products

G.I. Maltsev[1,2], E.V. Dokuchits[2], T.P. Minyukova[2]

[1]Novosibirsk State University, Novosibirsk, Russia
[2]Boreskov Institute of Catalysis, Novosibirsk, Russia

g.maltsev@g.nsu.ru

Emissions of carbon dioxide into the atmosphere, along with methane emissions, are the main cause of enhancing the greenhouse effect. To reduce the CO_2 content in the atmosphere, its injection into depleted gas fields and chemical binding with hydrogen to produce various valuable chemical products, including higher hydrocarbons and alcohols, are proposed.

In a two-stage reaction of CO_2 hydrogenation, carbon monoxide is formed in the first stage, and Fischer-Tropsch synthesis products are formed in the second stage. Iron-containing catalysts are the most active in this reaction and can be modified with potassium to reduce methane selectivity, cobalt to increase hydrocarbon yield, and manganese to increase selectivity towards light olefins [1,2].

The aim of this work is to determine the optimal composition of an iron-containing catalyst for the synthesis of higher C_{5+} hydrocarbons. Samples were synthesized by impregnation method with varying iron content (w_{Fe} = 2.5-10%), potassium (n_K/n_{Fe} = 0-0.60), cobalt (n_{Co}/n_{Fe} = 0.07-0.21), and manganese (n_{Mn}/n_{Fe} = 0.11-0.38). Aluminum oxide γ-Al_2O_3 was used as a carrier, which is readily available and has a high specific surface area.

Tests were conducted at a pressure of 2 MPa, 300-360°C, in a gas mixture of CO_2+$3H_2$. Pre-reduction was carried out in an H_2 atmosphere at a temperature of 450°C. The gas mixture flow rate was adjusted so that the CO_2 conversion rate on all samples fell within the range of 20-40%.

Catalytic tests showed that increasing the potassium content in the iron-containing catalysts reduced methane selectivity to as low as 10.2%, while selectivity towards higher hydrocarbons C_{5+} increased, reaching a maximum at a ratio of n_K/n_{Fe} = 0.6. Manganese modification led to a slight increase in selectivity towards olefins (up to 6.5%), accompanied by a sharp rise in selectivity towards undesired methane and carbon monoxide. Manganese modification using the chosen method proved to be ineffective and did not lead to an increase in selectivity towards desired products. Cobalt modification turned out to be the most promising. With a low cobalt content, a significant decrease in methane selectivity (7.1%) and an increase in selectivity towards higher hydrocarbons C_{5+} were observed, reaching a maximum at n_{Co}/n_{Fe} = 0.07. However, with an increase in cobalt content, methane selectivity significantly increased. The optimal ratio was found to be n_{Co}/n_{Fe} = 0.07. The specific catalytic activity of cobalt- and potassium-modified samples was twice that of samples modified with potassium alone.

The influence of the active component content in the sample on catalytic properties was investigated. A decrease in the active component content in samples modified with potassium alone led to a predominance of carbon monoxide in the products, as the preferential reaction on iron-containing samples is the first stage of CO_2 hydrogenation. For samples modified with potassium and cobalt, a decrease in the active component content led to an increase in selectivity towards higher hydrocarbons C_{5+}. The research showed that the most effective catalyst for CO_2 hydrogenation to obtain higher hydrocarbons C_{5+} is one deposited on γ-Al_2O_3, containing potassium with $n_K/n_{Fe} \geq 0.30$, cobalt with n_{Co}/n_{Fe} = 0.07, and an active component content of around 3%.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the framework of the state assignment of the Boreskov Institute of Catalysis SB RAS (project FWUR-2024-0033).

References

1. Jiang Y., Wang K., Wang Y., Liu Z., Gao X., Zhang J., Ma Q., Fan S., Zhao T.-S., Yao M., Journal of CO_2 Utilization, 2023, 67, 102321.
2. Minyukova T.P., Dokuchits E.V., International Journal of Hydrogen Energy, 2023, 48 (59), 22462–22483.

100-xPdxCu@UiO-66-NH_2 and 100-xPdxAu@UiO-66-NH_2 catalysts for selective 5-hydroxymethylfurfural reduction

D.P. Morilov, K.L. Timofeev, T.S. Kharlamova

Tomsk State University, Tomsk, Russia

ejsinov@mail.ru

Biomass provides a sustainable and environmentally friendly alternative to crude oil for producing valuable products [1]. 5-hydroxymethylfurfural (HMF) is an important biomass-based chemical platform, essential for the synthesis of a wide range of valuable products [2-4].

The present work focuses on an approach to control the properties of mono- and bimetallic 100-xPdxCu and 100-xPdxAu catalysts for the HMF reduction. The regulation of properties is achieved through the interaction with the functional groups of the Zr-based UiO-66-NH_2 metal-organic frameworks (MOFs) modified with NH_2 groups.

Catalysts designated as 100-xPdxCu@UiO-66-NH_2-Y and 100-xPdxAu@UiO-66-NH_2-Y, where Y denotes the fraction of amino terephthalate linkers, with 2 wt.% metal content were synthesized, with varying ratios of Pd (100-x) and Cu or Au (x) and using the adsorption properties of Zr-based MOFs towards Pd, Cu, and Au precursors which helped form metal particles mainly within the porous structure of the Zr-MOFs. The prepared samples were studied using XRD, low-temperature nitrogen adsorption, CO pulsed chemisorption, UV-visible spectroscopy, Raman spectroscopy, and IR spectroscopy. The catalytic properties were studied in cascade reactions of HMF reduction using the Parr 4560 reactor (Parr, USA) at 140–160 °C, 15 atm of H_2, HMF concentration of 0.05 mol/l, and HMF/metal molar ratio of 100. Specifically, the effect of functional groups of the Zr-MOF on the catalytic properties of monometallic Pd, Cu and Au samples based on UiO-66-NH_2-Y with different NH_2 were studied. Additionally, the influence of the Pd:Cu and Pd:Au ratios in bimetallic systems was studied using a series of samples based on UiO-66-NH_2-50, designated as 100-xPdxCu@UiO-66-NH_2-50 and 100-xPdxAu@UiO-66-NH_2-50.

Obtained results demonstrate that the approach used to control properties of 100-xPdxCu and 100-xPdxAu catalysts through the formation of heteroatomic bonds with the functional groups of the Zr-MOFs provides the potential for the purposeful design of new catalytic materials for the selective hydrogenation of HMF into valuable products. In particular, for the 100-xPdxCu catalysts, the preferential formation of metal particles/clusters in the porous space of the support was demonstrated due to the stabilization of the metal precursor with NH_2-groups of the Zr-MOF. The formation of bimetallic PdCu species was observed for the bimetallic samples based on UiO-66-NH_2-50, while individual Pd and Cu ones was observed for the bimetallic samples based on UiO-66-NH_2-100. Catalytic studies of the Pd@UiO-66-NH_2-Y samples with different NH_2 content indicated their high catalytic activity due to the high dispersion of Pd, with the maximum activity being observed for the Pd@UiO-66-NH_2-50 sample. Conversely, monometallic Cu@UiO-66-NH_2-Y exhibited low catalytic activity. Regardless of the presence of amino groups in the MOF and the composition of the active component, a distinguishing characteristic of the catalysts based on UiO-66-NH_2-Y was the formation of 2,5-dihydroxymethylfuran and 2,5-dihydroxymethyltetrahydrofuran as the main products, with a large contribution from deep hydrogenation products being observed for monometallic Pd catalysts. The Pd:Cu ratio in the bimetallic 100-xPdxCu@UiO-66-NH_2-50 catalysts additionally allows controlling the depth of the HMF reduction.

The results of the HMF reduction over obtained 100-xPdxCu and 100-xPdxAu catalysts will be presented, detailing the effect of the functional groups of the Zr-MOFs on the catalyst performance and providing insight into the reaction pathways of the HMF reduction over the studied catalysts.

This work was supported by the Russian Science Foundation, Grant 23-23-00173.

References

1. Choudhary V., Mushrif S.H., Ho C., Anderko A., Nikolakis V., Am. Chem. Soc., 2013, 135, 3997.
2. Chen S., Wojcieszak R., Dumeignil F., Marceau E., Royer S., Chem. Rev., 2018, 118, 11023.
3. Timofeev K.L., Vodyankina O.V., Reaction Chem. Engin., 2021, 6 (3), 418.
4. Kong X., Zhu Y., Fang Z., Kozinski J. A., Butler I. S., Xu L., Song H., Wei X., Green Chem., 2018, 20, 3657.

Photoactive composites $BiVO_4/TiO_2$-N and Bi_2WO_6/TiO_2-N in catalytic degradation of benzene

M.E. Morozova[1,2], M.N. Lyulyukin[1]

[1]Boreskov Institute of Catalysis, Novosibirsk, Russia
[2]Novosibirsk State University, Novosibirsk, Russia

m.morozova4@catalysis.ru

The use of photocatalysts makes it possible to convert the energy of sunlight into the energy for transformation of chemical bonds. This technology allows for a variety of chemical reactions to be carried out at mild conditions and room temperature. Moreover, it is possible to carry out photocatalytic processes that enhance environmental safety – photocatalytic degradation of harmful contaminants in air and water by oxidation. It provides an opportunity to convert all hydrocarbons – alcohols, ketones, and aldehydes, as well as aromatic compounds – into harmless CO_2 and H_2O. This method of purification is becoming more and more in demand by the air purifier industry. Using the new nitrogen-doped titanium dioxide (TiO_2–N), this process can be carried out not only under UV radiation (which is absorbed by the rutile or anatase phase of TiO_2), but also under visible light. The creation of composite material with heterojunction makes it possible to stabilize the activity of catalyst by redistribution of photogenerated charges between materials of this composite. It was shown that the introduction of bismuth tungstate Bi_2WO_6 ($Eg = 2.8$ eV) stabilizes the activity of the TiO_2–N-based catalyst under visible light [1].

One of the most harmful volatile organic compounds, benzene, has a feature of formation of carbon deposits on the surface of photocatalysts during the process. This causes the blocking of active sites and therefore the activity of the catalyst decreases. TiO_2–N has a sufficiently high activity under visible light, however, with an increase in the concentration of benzene, its activity decreases as well. In this work, the activity of composite systems based on nitrogen-doped titanium dioxide and bismuth vanadate $BiVO_4$ ($Eg = 2.4$ eV) in the reaction of benzene degradation was studied. The aim of this work was the investigation of activity of these systems and relation between the concentration of benzene and amount of carbon deposits formed for a series of Bi_2WO_6/TiO_2-N and $BiVO_4/TiO_2$-N samples.

The nitrogen-doped titanium dioxide was synthesized according to the previously published procedure [2] using the hydrolysis of titanyl sulfate with an aqueous ammonia solution. Bi_2WO_6, $BiVO_4$ and their composites with TiO_2-N were prepared by the hydrothermal synthesis [3]. The as-obtained samples were characterized by UV-Vis diffuse reflectance spectroscopy (DRS), X-ray photoelectron spectroscopy (XPS) and photoelectrochemical methods. The photoactivity of samples in the reaction of benzene vapor decomposition under UV and blue irradiations was studied in a continuous-flow setup equipped with a long-pass gas cell for IR spectroscopic analysis of gas-phase concentration of benzene, CO_2, and CO. The activity of photocatalysts was estimated from the steady-state rate of CO_2 formation (μmol/min). The photocatalysts were irradiated using LEDs with the emission spectra maxima at 441 nm (referred to as Vis) and at 370 nm (referred to as UV). The amount of carbon deposits was detected by total organic carbon analyzer using a unit for solid-sample analysis.

Composites with $BiVO_4$ demonstrate a distinctly higher light absorption at 375–500 nm than the Bi_2WO_6-containing samples. The activity of Bi_2WO_6/TiO_2–N composites depend on the amount of bismuth tungstate and has a descending character with a local maximum at 30% content. Samples with a low $BiVO_4$ content are more active among a series of $BiVO_4$-containing samples.

This work was supported by the Russian Science Foundation, Grant No. 23-23-00505 (https://rscf.ru/project/23-23-00505/).

References

1. Lyulyukin M., et al., IJMS, 2023, 24, 6, 5693.
2. Kovalevskiy N., et al., Nanomaterials, 2022, 12, 23, 4146.
3. Lyulyukin M.N., et al., J. Struct. Chem., 2024, 65, 2, 341–354.

Ag-Cu/CeO_2-ZrO_2-SnO_2 catalysts for CO and soot oxidation

A.M. Murtazalieva, M.V. Chernykh, M.V. Grabchenko, G.V. Mamontov, M.A. Salaev

Tomsk State University, Tomsk, Russia

murtazalieva.anka@yandex.ru

Emissions of particulate matter (soot) and CO from industrial plants and motor vehicles have recently become a serious ecological problem. Such emissions have a direct negative impact on human health and the environment [1]. These pollutants react with atmospheric gases, moisture in the presence of sunlight to form other more toxic substances, which in turn are the main reason for smog and acid rains, destruction of ozone layer. Currently, chromium-containing catalysts [2] or catalysts based on noble metals (Pd, Pt, Au) [3] are known. Therefore, the development of high-performance affordable and environmentally friendly catalysts for low-temperature total oxidation of harmful compounds is still challenging.

The aim of this work was to synthesize and study the CeO_2-ZrO_2-SnO_2-supported Ag-Cu catalysts for CO and soot oxidation. A series of CeO_2-ZrO_2-SnO_2 mixed oxide systems was prepared by sol-gel method using citric acid as a chelating agent with varying molar ratios of Ce/Zr, Ce/Sn, and Zr/Sn: $Ce_{0.67}Sn_{0.33}O_2$, $Ce_{0.33}Sn_{0.67}O_2$, $Sn_{0.67}Zr_{0.33}O_2$, $Sn_{0.33}Zr_{0.67}O_2$, $Ce_{0.6}Zr_{0.4}O_2$, $Ce_{0.4}Sn_{0.35}Zr_{0.25}O_2$, and $Ce_{0.19}Sn_{0.68}Zr_{0.13}O_2$. Ag-Cu catalysts were prepared on the best-performing oxide supports by wet impregnation from the water solutions of $AgNO_3$ and $Cu(NO_3)_2 \times 3H_2O$ followed by drying and calcination at 300°C. The total content of Ag and Cu was no more than 2 wt.%.

The prepared supports and catalysts were studied by a complex of physical-chemical methods, including low-temperature N_2 sorption, X-ray fluorescence analysis (XRF), X-ray diffraction (XRD), Raman spectroscopy, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), temperature-programmed H_2 reduction (TPR-H_2). The catalytic activity of materials was studied in the processes of CO and soot oxidation.

The TEM, XRD and Raman spectroscopy data show that large SnO_2 particles with a sufficiently low concentration of oxygen vacancies are localized on the surface in ternary oxide systems. These particles are in close contact with solid solutions based on CeO_2 as well as tetragonal ZrO_2 and/or $Ce_xZr_{1-x}O_2$. The resulting multiple interfacial boundaries become active sites for the CO oxidation and soot combustion.

The report will examine the textural and structural characteristics of bimetallic Ag-Cu catalysts and discuss the key principles that determine the catalytic properties of supported catalysts in reactions of CO and soot oxidation.

This work was supported by the Russian Science Foundation, Grant № 23-73-00109, https://rscf.ru/project/23-73-00109/.

References

1. Legutko P., Stelmachowski P., Yu X., Zhao Z., Sojka Z., Kotarba A., ACS Catal., 2023, 13, 3395–3418.
2. Venkataswamy P., Jampaiah D., Rao K.N, Reddy B.M., Appl. Catal. A, 2014, 488, 1–10.
3. Gao Y.X., Duan A.Q., Liu S., Wu X.D., Liu W., Li M., Chen S.G., Wang X., Weng D., Appl. Catal. B, 2017, 203, 116–126.

Cyclohexanone synthesis via phenol and cyclohexanol transfer hydrogenation

A.A. Philippov, N.S. Nesterov, O.N. Martyanov

Boreskov Institute of Catalysis, Novosibirsk, Russia

philippov@catalysis.ru

Transfer hydrogenation (TH) represents a promising approach for hydrogen-free hydrogenation, in which simple organic molecules such as lower aliphatic alcohols can be employed as reducing agents [1,2]. Among the heterogeneous catalysts available, metal nickel is one of the most widely used due to its excellent activity and availability [3]. Concurrently, the utilization of primary alcohols in conjunction with nickel-based catalysts has been observed to result in catalyst deactivation, as aldehydes formed through primary alcohol dehydrogenation participate in the formation of CO, which is subsequently disproportionated to elemental carbon and CO_2 [4]. Consequently, secondary alcohols, particularly 2-PrOH, have been identified as promising hydrogen donors when employed in conjunction with Ni-based catalysts.

The crucial matter of TH is the low-value products formed from hydrogen donors, which are typically employed in excess. For instance, the dehydration of 2-PrOH results in acetone formation, which is not very valuable product despite the fact that this molecule is extensively utilized in numerous applications. At the same time, the recovery procedure necessitates the use of H_2, which contravenes the principles of TH. Conversely, some secondary alcohols can be dehydrogenated into ketones, which are highly demanded in industry. For instance, cyclohexanone, which serves as a precursor for polyamide synthesis [5], can be produced from cyclohexanol through TH [6]. This process has a cumulative effect when phenol is used as a hydrogen acceptor, as both the hydrogen donor and acceptor are transformed into cyclohexanone. It is also important to note that phenol demonstrates high reactivity in Ni-catalyzed TH due to the presence of an OH-group, which facilitates adsorption of the molecule on the catalyst surface [7].

This work describes the TH of phenol and cyclohexanol over Raney nickel and Ni/Al_2O_3 at different temperatures and cyclohexanol-to-phenol ratios. The latter catalyst was prepared by a promising method based on coprecipitation of catalyst precursors in supercritical CO_2. This synthetic approach allows for the achievement of a high nickel content, up to 90 mass%, which is comparable to that of Raney nickel. It also maintains high dispersion of the active compound and high thermal stability, in comparison to Raney catalysts. Both Raney nickel and Ni/Al_2O_3 demonstrate limited activity in the TH of phenol and cyclohexanol at temperatures below 200 °C. This can be attributed to the strong adsorption of phenol on the catalyst surface. Conversion of phenol reaches 86% at 200 °C and a cyclohexanol-to-phenol molar ratio of 10:1. Decreasing the ratio to 5:1 and 2:1 results in lower phenol conversion, reaching 71% and 56%, respectively. It is also important to note that the ratio of 2:1 between cyclohexanol and phenol is stoichiometric for the synthesis of cyclohexanone.

This work was supported by the Russian Science Foundation (grant 24-23-20044) and the Government of the Novosibirsk region (grant p-86).

References

1. Park Y.K., Ha J.M., Oh S., Lee J., Chem. Eng. J., 2021, 404, 126527.
2. Xu H., Li H., J. Energy Chem., 2022, 73, 133–159.
3. Gilkey M.J., Xu B., ACS Catal., 2016, 6, 1420–1436.
4. Nesterov N., Philippov A., Pakharukova V., Gerasimov E., Yakushkin S., Martyanov O., Chinese J. Catal., 2024, 58, 168–179.
5. Kong X., Gong Y., Mao S., Wang Y., ChemNanoMat, 2018, 4, 432–450.
6. Zhu Z., Yang L., Ke C., Fan G., Yang L., Li F., Dalt. Trans., 2021, 50, 2616–2626.
7. Philippov A., Nasokhov D., Prosvirin I., Martyanov O., Mol. Catal., 2024, 561, 114200.

Ag- and Pt-containing catalysts based on mixed CeO_2-Fe_2O_3 oxides for deep toluene oxidation

D.A. Ponizovnaya, A.S. Savel’eva, G.V. Mamontov

Tomsk State University, Tomsk, Russia

dianakirmas@gmail.com

The increase in emissions of volatile organic compounds (VOCs) poses a great danger to the environment and human health. Toluene is a common VOCs with high volatility and toxicity to living organisms. An effective method of neutralizing toluene is deep catalytic oxidation on noble metals (Pt, Pd, Au, Ag). Transition metal oxides (CeO_2, FeO_x, MnO_x, etc.) are used as supports for catalysts, which can also exhibit catalytic activity. Recently, there has been a lot of attention paid to the interaction between the deposited component and the support, as well as the influence of this factor on the catalytic properties of deposited catalysts.

The aim of this work was to establish the influence of the physical and chemical properties of mixed Ce-Fe oxide supports on the structure and catalytic properties of deposited Ag and Pt catalysts in the deep oxidation reaction of toluene.

Oxide carriers were prepared using the citrate method with $Ce(NO_3)_3*6H_2O$ and $Fe(NO_3)_3*9H_2O$ as metal oxide precursors. After drying and calcining the samples at 550 °C, individual CeO_2 and Fe_2O_3 and mixed oxides with different molar ratios of Ce and Fe were obtained, designated as xCeyFe, where x and y are the molar content. Ag-containing catalysts were obtained by incipient wetness impregnation from $AgNO_3$ solution. Similarly, platinum catalysts were prepared. The silver and platinum content were from 2 to 5 %. All samples were characterized by low-temperature N_2 adsorption, XRD, Raman spectroscopy, TPR-H_2, TEM, and catalytic properties were investigated in toluene oxidation reaction.

The XRD method established that CeO_2 crystallizes in a cubic phase with a fluorite structure (PDF 43-1002), and iron oxide is represented by large crystals of the Fe_2O_3 hematite phase (PDF 24-0072). No solid solutions were found in mixed systems and a decrease in the size of crystallites CeO_2 and Fe_2O_3 are observed. Weak intensity reflexes corresponding to the hematite phase are observed in the 1Ce6Fe sample, the specific surface area of the sample is 74 m^2/g. All other samples have a specific surface area of 23-55 m^2/g.

The TPR-H_2 CeO_2 profile is characterized by two regions of reduction. In the range of 300 – 650 °C, the reduction of ceria surface oxygen observed, a peak above 750 °C may be associated with the reduction of the bulk phase of CeO_2 to Ce_2O_3. The TPR-H_2 profile for Fe_2O_3 is characterized by two maxima, which are attributed to the sequential reduction of Fe_2O_3 to Fe_3O_4 (at 385 °C) and Fe_3O_4 to FeO (at 634 °C), while H_2 absorption is observed also at temperatures above 700 °C. For mixed oxides, a two-peak reduction pattern is observed in the region up to 500 °C and an increase in the total amount of absorbed H_2. This is probably due not only to the reduction of dispersed Fe_2O_3, but also to an increase in the ability of the surface of CeO_2 to recover in the presence of iron oxide and the formation of a larger number of oxygen vacancies that increase catalytic activity, which is confirmed by Raman spectroscopy data. The interaction of Ag and Pt with the surface of oxides helps to reduce the recovery temperature of samples and to increase the consumption of hydrogen.

Oxides, Ag and Pt catalysts based on them have been investigated in the toluene oxidation reaction. It was found that CeO_2 is the most active, and the activity of mixed systems and Fe_2O_3 is significantly lower and comparable to each other. However, with the introduction of Ag and Pt on the surface of the carrier, the temperature of 50% toluene conversion decreased, for the Ag and Pt catalysts based on 1Ce6Fe support this effect was the most significant.

Thus, Ag and Pt catalysts demonstrate improved catalytic properties in deep toluene oxidation compared to supports due to the interaction of metals with the CeO_2-Fe_2O_3 surface and the appearance of a synergistic effect consisting in increasing the reactivity of the samples.

This work was supported by the Russian Science Foundation, Grant № 23-73-10152.

Ni-based catalysts on $LaCeO_x$ supports modified with Pr_6O_{11} for dry reforming of methane

P.K. Putanenko, N.V. Dorofeeva, M.V. Grabchenko, O.V. Vodyankina

Tomsk State University, Tomsk, Russia

putanenko.p@mail.com

Ni-based catalysts for dry reforming of methane (DRM) are widely used as less expensive alternative to noble metals with similar activity. However, such materials tend to suffer from severe coking under exposure to CH_4, which leads to their rapid deactivation. Therefore, to implement the DRM, the stability of Ni-based catalysts must be ensured. One of the common approaches to this problem is to deposit metal particles on supports that can sustain high dispersion of particles and activate reagents for better coking resistance [1, 2]. The supports with good redox properties can favor the oxidation of the formed carbon products, which can help sustaining the catalyst stability. Ceria-based material with high amount of oxygen vacancies are promising materials for such process. It was shown that doping ceria with different cations can increase the oxygen vacancy concentration [3].

In the present work we studied the structural and functional properties of Ni-based DRM catalysts on mixed La_2O_3-CeO_2-Pr_6O_{11} oxides prepared by citrate method. The Ce/La ratio was chosen to be 1 or 5, the Pr content varied from 1 to 10 mol.%. Structure of samples and their surface properties were characterized by XRD, TPD-CO_2, TPR-H_2, and Raman spectroscopy. Catalytic properties in DRM process were studied in tubular fixed bed reactor in the temperature range from 400 to 800 °C. Stability of the catalysts was studied at 650 °C. Structure and quantity of coking products after stability tests were characterized by Raman spectroscopy and STA.

According to the XRD data, all samples feature fluorite structure of CeO_2 with enhanced lattice parameter which indicates the formation of substitutional solid solution. NiO phase is formed as a precursor of active component (Ni^0) after wet impregnation. Raman spectra of the samples show the presence of F_{2g} band at ~440 cm^{-1} typical of fluorite structure and D-band at ~580 cm^{-1} indicating the presence of oxygen vacancies associated with the presence of dopants. The observed enhancement of the D-band intensity for 532 nm excitation wavelength can be attributed to the Raman resonance effect for the Pr-doped ceria and indicates the change in the Pr^{4+}/Pr^{3+} ratio [4], which will be discussed in the report.

All samples show similar activity in the temperature range of 400-800 °C and H_2/CO ratio close to 1 in the range of 600-800 °C. The sample with 5 mol.% Pr shows higher stability and initial activity both in terms of CH_4 and CO_2 conversions as well as H_2/CO ratio compared to 1 mol.% Pr. For example, the CH_4 conversion for 5 mol.% Pr sample decreased by 11% from the initial value while for 1 mol.% Pr. sample it was 20%. A decrease in activity during the stability tests is attributed to coking of the catalysts.

Basic properties, reducibility of NiO in the samples, quantity and properties of coking products as functions of Pr content as well as Ce/La ratio will be discussed in the report in details.

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

References

1. Pakhare D., Spivey J., Chem. Soc. Rev., 2014, 43, 7813–7837.
2. Aramounia N.A.K., Toumab J.G., Tarbousha B.A., et al., Renew. Sustain. Energy Rev., 2018, 82, 2570–2585.
3. Schmitt R., Nenning A., Kraynis O., et al., Chem. Soc. Rev., 2020, 49, 554–592.
4. Westermann A., Geantet C., Vernoux Ph., Loridant S., J. Raman Spectrosc., 2016, 47, 1276–1279.

Development of advanced methods for recycling polymer waste in anhydrous reducing media

A.S. Romanov, N.S. Nesterov, O.N. Martyanov

Boreskov Institute of Catalysis, Novosibirsk, Russia

chemonelove@mail.ru

Currently, the problem of processing organochlorine compounds is becoming increasingly relevant. The main sources of organochlorine pollutants are PVC-based plastics, agricultural pesticides, and solvents used in textile degreasing and the pharmaceutical industry. Traditional methods of recycling polymer waste, such as pyrolysis or incineration, have limitations on the chlorine content of the polymer waste mixture or are not applicable. It is necessary to propose the basic principles for the development of technologies for the processing of organochlorine compounds.

One of the most actively developing approaches to the utilization of organochlorine pollutants is reductive transformations leading to hydrogenolysis of the C-Cl bond [1]. The reducing agent in these processes can be both gaseous hydrogen [2] and various compounds acting as hydrogen donors [3, 4]. In most cases, hydrodechlorination processes with hydrogen gas are carried out in the presence of heterogeneous catalysts, which are often systems based on Pd, Pt, Au, Fe_2O_3, zeolites [5], as well as mixed Ni-Mo containing sulfides [6]. An important aspect of hydrodechlorination processes is the use of hydrochloric acid scavengers, which is the main product of the ongoing transformations. Both inorganic scavengers such as $CaCO_3$, NaOH [7], NH_3, etc. and organic scavengers such as Et_3N, $C_5H_{11}N$ can be used. It should be noted that studies on the effect of HCl absorbers on the kinetics of the hydrodechlorination process are rather limited.

In this work, the use of alcohols as hydrogen donors for the reduction of organochlorine compounds is proposed, since the use of molecular hydrogen has certain risks and limitations, such as explosion hazard, metal corrosion, etc. Applied Ni-Mo sulfide systems, which are well known for their use in the field of hydrotreating oil fractions, will be used as catalysts. Currently, there are no data in the literature on the use of Ni-Mo sulfide catalytic systems for hydrodechlorination processes where alcohols would act as hydrogen donors.

Keywords: hydrogen transfer reaction; heterogeneous catalysts; organochlorine compounds; chlorobenzene; dechlorination.

The work was carried out with the support of the Russian Science Foundation (project no. 24-23-20054, https://rscf.ru/project/24-23-20054 /) the Government of the Novosibirsk region (grant p-80).

References

1. Gorbunova T.I., Saloutin V.I., Chupakhin O.N., Russian Chemical Reviews, 2010, 79, 6, 511–530.
2. Kume A., et al., Appl. Catal. B., 2008, 81, 3–4, 274–282.
3. Pittman C., J. Hazard. Mater., 2001, 82, 3, 299–311.
4. Wu W., et al., Chemosphere, 2005, 60, 7, 944–950.
5. Keane M.A., Journal of Chemical Technology & Biotechnology, 2007, 82, 9, 787–795.
6. Gryglewicz G., et al., Chemosphere, 2006, 62, 1, 135–141.
7. Lu J., et al., Waste Management., 2019, 99, 31–41.

Synthesis and investigation of NiO-$CuO/Al(OH)_3$ catalysts in the catalytic pyrolysis of methane

D.M. Shivtsov[1,2], Y.I. Bauman[1], G.B. Veselov[1], E.V. Shelepova[1], A.B. Ayupov[1], Y.V. Shubin[2,3]

[1]*Boreskov Institute of Catalysis, Novosibirsk, Russia*
[2]*Novosibirsk State University, Novosibirsk, Russia*
[3]*Nikolaev Institute of Inorganic Chemistry, Novosibirsk, Russia*

danil@catalysis.ru

Hydrogen is an essential reagent used for refining, chemicals, transport, electricity generation and etc. At the same time, it is considered as a promising environmentally friendly energy source. There are many ways to produce hydrogen. However, the most prospective technology in foreseeable future is the methane pyrolysis – an approach to produce hydrogen without the CO_2 formation [1]. Methane is the main component of natural gas – the widespread resource with a low cost. There are two ways to carry out the methane pyrolysis: catalytic and non-catalytic. The first one is more attractive due to a decrease of the reaction temperature along with significantly increase of products yield. Besides hydrogen, the second product formed in the process of catalytic methane decomposition is carbon nanomaterial [2]. Unlike the thermal pyrolysis process, structured carbon is formed in the presence of catalysts. Nanostructured carbons with unique physical and chemical characteristics can be used in various applications such as sorption, electrochemistry, catalysis, etc.

In the last few years, a wide range of catalysts in various aggregate states has been used for the catalytic pyrolysis of methane: molten or solid. The first ones are resistant to deactivation by coke, however the latter are the simplest in terms of implementing the process [3]. The most active compounds in the process of catalytic pyrolysis are metal-containing catalysts, based on Ni, Co and Fe. The Ni-containing systems are effective already at temperatures about 550 °C. The performance of nickel-based catalysts in terms of activity, stability and durability can be improved by doping with a second metal compound, for example, such as copper [4]. The introduction of copper into the composition of Ni-containing catalysts improves the textural characteristics of the catalysts. Highly dispersed oxides or hydroxides with a developed porous structure, such as Al_2O_3, $Al(OH)_3$, MgO and others, are used as promoters [5]. Another factor affecting on the catalyst activity is the synthesis method. Mechanochemical activation methods are popular for the synthesis of a wide variety of materials. In addition to the absence of solvents, one of the advantages of the method is the simplicity and the possibility of preparing large volumes of the target material. This method allows one to synthesize compounds ranging from conventional metal alloys to mixed oxides.

Thus, in our research, NiO-$CuO/Al(OH)_3$ catalysts were synthesized by the mechanochemical activation method and were investigated in the process of methane catalytic pyrolysis. Such parameters as the diameter of the grinding media, radial speed, and synthesis time were varied. The obtained catalytic systems were investigated by physico-chemical methods: XRD, granulometric analysis, TPR-H_2 and so on. During the study, the efficiency of the catalytic methane decomposition over the NiO-$CuO/Al(OH)_3$ catalyst was studied. The maximum hydrogen yield ~140 $Nm^3/(kg_{cat}\cdot h)$ is attained at 650 °C. The report will contain in detail the effect of mechanochemical activation on the phase composition of the catalyst and its effect on the methane pyrolysis process.

This study was funded by the Russian Science Foundation (grant number 24-29-20095 of April 12, 2024; https://rscf.ru/en/project/24-29-20095/, BIC SB RAS) in cooperation with the Government of the Novosibirsk Region (agreement No. r-87 of March 22, 2024; BIC SB RAS).

References

1. Abbas H.F., et.al. Int. J. Hydrog. Energy, 2010, 35, 1160–1190.
2. Pudukudy M., et.al. Appl. Catal. B, 2017, 218, 298–316.
3. Patlolla S.R., et.al. Renew. Sust. Energ. Rev., 2023, 181, 1–12.
4. Cazaña F., et.al. Chem. Eng. J., 2022, 6, 1–20.
5. Takenaka S., et.al. Appl. Catal. A-Gen., 2001, 217, 101–110.

Photoactive self-cleaning materials for inactivation and destruction of biological contaminants

M.I. Solovyeva[1,2], E.S. Zhuravlev[3], G.A. Stepanov[3], M.V. Sergeeva[4], Y.N. Kozlova[3], A.V. Bardasheva[3], V.V. Morozova[3], V.A. Richter[3], D.V. Kozlov[1,2], D.S. Selishchev[1,2]

[1]Boreskov Institute of Catalysis, Novosibirsk, Russia
[2]Novosibirsk State University, Novosibirsk, Russia
[3]Institute of Chemical Biology and Fundamental Medicine, Novosibirsk, Russia
[4]Smorodintsev Research Institute of Influenza, Saint-Petersburg, Russia

smi@catalysis.ru

The problem of the spread of dangerous infections through contaminated surfaces has escalated during the last pandemic due to COVID-19. This has underlined the need to create materials capable of independently cleaning their own surface from pathogenic bacteria and viruses. One promising way to obtain these materials is to modify its surface with photocatalysts, which completely oxidize chemical compounds and contribute to the destruction of bacteria and viruses under light [1].

The new method to obtain such materials included the following stages: preparation of a mixture consisting of nanocrystalline nitrogen-doped titanium dioxide [2], titanium (IV) isopropoxide [3] or silicon binder [4] fixing photocatalyst particles, and isopropyl alcohol as a solvent; impregnation with the mixture; drying at room temperature to remove the solvent and washing with water. This method allowed us to obtain photoactive coatings on the surfaces of different materials such as fabric, glass, and metal.

The antibacterial activity of the materials was studied using *E. coli* and *S. aureus*. Only 12% of living cells of *E. coli* and 22% of *S. aureus* remained on the material after 30 min of UVA irradiation (365 nm, 8 mW cm^{-2}). The difference in the rate of cell death is due to the differences in the structure of bacterial cell wall. Changes in bacterial cell structures after UVA irradiation on the surfaces of materials were observed using SEM.

Antiviral properties were studied using the example of enveloped and non-enveloped viruses using the influenza A/PR/8/34 virus (H1N1) and the bacteriophage PA136, respectively. The infectivity of the influenza virus rapidly decreased within 20 min on the surface of the photoactive fabric under UVA radiation (8 mW cm^{-2}). In the case of bacteriophage, the death of 83% of the viral particles was shown after 1 h of irradiation (450 nm, 60 mW cm^{-2}), and complete inactivation occurred within 6 h. At the same time, a significant decrease in concentration of bacteriophage DNA was detected by polymerase chain reaction (PCR), confirming the destruction of all virus structures.

Additionally, the investigation in the destruction of *C. albicans* showed that the obtained photoactive material had antifungal properties. All cells died after 2 and 3 h under visible light (442 nm, 30 mW cm^{-2}) and UVA irradiation (365 nm, 8 mW cm^{-2}), respectively. Thus, the material can destroy objects that are resistant to adverse conditions.

Since pathogenic bacteria can keep and transport antibiotic resistance genes even after their death, the degradation of nucleic acids was investigated. It was shown that DNA fragments with length 71–454 bp to be rapidly destroyed on the surface of these materials. An increase in the length of the fragment leads to an increase in its destruction efficiency. The obtained results show the potential of using these materials for permanently cleaning surface from various macromolecules and biological objects under light.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the governmental assignments for Boreskov lnstitute of Catalysis (project FWUR-2024-0036) and Novosibirsk State University (№ 122122100147-9).

References

1. Solovyeva M., et al., Chem. Eng. J., 2020, 388, 124167.
2. Kovalevskiy N., et al., Nanomaterials, 2022, 12, 359.
3. Selishchev D., et al., Catalysts, 2022, 12, 1298.
4. Selishchev D., Stepanov G., Solovyeva M., Zhuravlev E., Richter V., Kozlov D., Patent RU2793180, 2023.

A selective design of nanostructured Ru/C catalysts for a complex processing of plant biomass into valuable chemical products

V.V. Sychev[1], A.V. Miroshnikova[1], A.S Kazachenko[1], V.E. Tarabanko[1], O.P. Taran[1,2]

[1]Institute of Chemistry and Chemical Technology, Krasnoyarsk, Russia
[2]Boreskov Institute of Catalysis, Novosibirsk, Russia

sychev.vv@icct.krasn.ru

Reductive catalytic fractionation (RCF) is the one of promising methods of plant biomass valorization, which includes the catalytic depolymerization of lignin and hemicelluloses, as well as the isolation of a solid cellulose product [1, 2]. Depolymerization of lignin allows to obtain valuable aromatic compounds - methoxyphenols. Among the promising compounds obtained from the polysaccharide part of lignocellulosic biomass, one can highlight γ-valerolactone - a green solvent and feedstock for the production of biopolymers, biofuels, used in both the food and pharmaceutical industries. γ-Valerolactone and its derivatives can also be used as fuel additives.

For hydrogenation processes within the RCF, solid catalysts based on Ru are of greatest interest, since in aqueous and aqueous-alcoholic media it exhibits the greatest activity compared to other platinum metals [2, 3].

The goal of the study is to develop solid bifunctional catalysts based on ruthenium nanoparticles deposited on the mesoporous graphite-like carbon material (CM) Sibunit-4 for valorization of lignocellulosic biomass components into valuable chemical products.

It has been established that the presence of the catalyst in the process of flax shives RCF increases the yield of methoxyphenols by more than 10 times (up to 12 wt.%), compared with a non-catalytic experiment. The selective design of the Ru-catalyst - introducing acidic properties to the support, allows increasing the yield of methoxyphenols by more than 2 times, compared with the Ru-catalyst based on unoxidized CM (process conditions: 3 g flax shives, 0.3 g cat.; 40 mPa H_2, ethanol 60 ml, 250°C) [4].

In the hydrogenation of levulinic acid to γ-valerolactone, an increase in the acidity of the catalyst negatively affects the yield of the target product. The maximum selectivity of the process of hydrogenation of levulinic acid to γ-valerolactone in an aqueous medium (yield > 98 mol.%) is achieved when using catalysts characterized by slightly alkaline pH values) (process conditions: 2.5 g levulinic acid, 0.125 g cat.; 1.2 MPa H_2, H_2O 50 ml, 160°C) [5].

Thus, the effectiveness of Ru catalysts based on CM Sibunit-4 is demonstrated, as well as the multidirectional influence of the acidity of the support depending on the investigated process.

This work was supported by the Russian Science Foundation, Grant 21-73-20269.

References

1. Ross K., Giuseppe M., International Journal of Molecular Sciences, 2010, 11, 1544–1558.
2. Galkin M.V., Samec J.S., ChemSusChem. 2016, 9, 13, 1544–1558.
3. Alonso D.M., Wettstein S.G., Dumesic J.A., Green Chem., 2013, 15, 584.
4. Taran O.P., Miroshnikova, A.V., et. al., Catalysts, 2022, 12, 1384
5. Sychev V.V., Baryshnikov S.V., et.al. J. Sib. Fed. Univ. Chem., 2021, 14, 1, 5–20.

The role of support acid-base properties on aerobic oxidation of 5-hydroxymethylfurfural over oxide-supported AuPd catalysts

K.L. Timofeev, T.S. Kharlamova, O.V. Vodyankina

Tomsk State University, Tomsk, Russia

kvintkl@gmail.com

2,5-furandicarboxylic acid (FDCA) is an important monomer to produce biodegradable polymers. It is used for production of polyethylenefuranoate (PEF), a “green” alternative to polyethylene terephthalate (PET). The great attention to FDCA is caused by the opportunities to use renewable sources such as biomass for its production. Thus, FDCA can be produced by catalytic aerobic oxidation of biomass-derived 5-hydroxymethylfurfural (5-HMF) [1].

Different catalytic systems can be used for 5-HMF oxidation to FDCA, but catalysts based on noble metals such as Au, Pd, Ru, and Pt have significant advantages due to their chemical and thermal stability, and high activity and selectivity. The most efficient catalysts contain Au, but they require strong alkaline medium (pH > 12, NaOH) to convert 5-HMF to FDCA [2]. The Pd addition as a second component was shown to result in bimetallic AuPd alloy system to perform efficiently even under pH ~8 of the reaction media due to synergistic effect accompanied by a change in the reaction pathway of the HMF conversion via oxidation of primarily OH group [3]. In addition, the support nature can strongly affect the catalytic properties of catalysts, which makes it possible to further control their performance. Particularly, support acid-base properties were shown to play a significant role in the 5-HMF conversion over supported Au catalyst via oxidation of primarily aldehyde group to form 5-hydroxymethyl-2-furancarboxylic acid (HMFCA) [4, 5]. However, for bimetallic AuPd alloy catalysts, which are characterized by the change in the HMF oxidation pathway [3], the role of the support acid-base properties remains unclear.

This work is focused on the effect of support acid-base properties on aerobic oxidation of 5-HMF over bimetallic AuPd/$Ce_xZr_{1-x}O_2$ and AuPd/$Ce_xLa_{1-x}O_2$ catalysts. The $Ce_xZr_{1-x}O_2$ and $Ce_xLa_{1-x}O_2$ oxides were prepared by the citrate sol-gel method. The supported bimetallic catalysts were prepared by impregnation reduction technique. Additionally, colloidal AuPd nanoparticles (NPs) were obtained via pulsed laser ablation [3]. The prepared samples were characterized by XRD, electrophoretic light scattering, adsorption of acids and bases from aqueous solutions, TPD-NH_3, etc. The catalytic properties of the samples were studied using the Parr 5500 HR reactor, with the reaction mixture being analyzed by HPLC.

The results showed that HMF oxidation occurred predominantly via the hydroxyl group to form 2,5-diformylfuran (DFF) followed by its rapid oxidation to formyl-furan-carboxylic acid (FFCA) for all bimetallic catalyst studied. However, for the colloidal AuPd catalyst, the FFCA was the main product of the cascade reaction because the final stage of the FFCA oxidation to FDCA was characterized by a low rate. In contrast, high FDCA yield was observed for all supported samples. The support nature did not strongly contribute to the catalytic activity of the AuPd catalysts towards HMF oxidation, but it strongly affected the subsequent FFCA oxidation to FDCA. Thus, AuPd/$Ce_xZr_{1-x}O_2$ samples showed similar catalytic activity (specific rate constants of HMF oxidation were ~8×10^{-5} s^{-1} mol^{-1}), but the FDCA yield increased in the series of samples AuPd/ZrO_2 (36%) < AuPd/$CeZrO_x$ (72%) < AuPd/CeO_2 (86%). The effect of the acid-base properties of the $Ce_xZr_{1-x}O_2$ and $Ce_xLa_{1-x}O_2$ supports on the catalytic properties of the supported AuPd catalysts will be discussed in detail.

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

References

1. Zhang X., et al., Journal of Energy Chemistry, 2018, 27, 73–85.
2. German D., Pakrieva E., Kolobova E., et al., Catalysts, 2021, 11, 115–135.
3. Timofeev K.L., et al., Appl. Catal. A, 2023, 656, 119121.
4. Megías-Sayago C., Chakarova K., Penkova A., et al., ACS Catal., 2018, 12, 11154–11164.
5. Q. Li, H. Wang, Z. Tian, et al., Catal. Sci. Technol., 2019, 9, 1570–1580.

Polysaccharides valorization over solid acid catalyst; doping of mesoporous silica SBA-15 with Al and Zr to increase acidity

Yu.A. Trotsky[1], A.O. Eremina[1], S.A. Novikova[1], V.V. Sychev[1,2], O.P. Taran[1,2,3]

[1]Institute of Chemistry and Chemical Technology SB RAS, Krasnoyarsk, Russia
[2]Siberian Federal University, Krasnoyarsk, Russia
[3]Boreskov Institute of Catalysis, Novosibirsk, Russia

trockiy.ya@icct.krasn.ru

The formation of abundant plant biomass waste is a present problem in agriculture and wood industry, which requires the development of new waste-free technologies to obtain products with high added value [1]. For example, the most common wood in Russia is larch, which contains arabinogalactan (AG) in large quantities [2]. During depolymerization of arabinogalactan, high-value monomeric compounds are formed, namely: arabinose, galactose, furfural and 5-hydroxymethylfurfural (5-HMF), covering a wide range of industrial applications [3]. To ensure a high yield of products, it is necessary to choose a suitable catalyst. The microporosity of SBA-15 helps to reduce diffusion limitation in liquid phase reaction, doping of silica with Al and Zr oxides allows us to introduce acidity, necessary for effective depolymerization [4].

The aim of this work is to develop solid catalysts based on mesoporous silicate SBA–15 doped with Al and Zr oxides and evaluate them in AG depolymerization reaction to obtain high-value added monomeric products.

A series of SBA-15 based catalysts with different ratios of metal oxides Al/Zr (0.5; 1.0; 2.0) was synthesized and studied by XRF, XPS, TEM, SEM, N_2-adsorption-desorption, pH_{pzc}. A decrease in textural characteristics was observed with an increase in the content of dopants. Via pH_{pzc} measurements determined that Al/Zr ratio of 0.5 provides maximum acidity of the catalyst (pH_{pzc} of 2.5Al-5Zr-SBA-15 = 2.43), ensuring the most effective AG depolymerization.

The maximum yield of monomers – 61 wt.% was achieved within 4 h. The maximum content of the target products, namely arabinose and galactose, is 4.55 wt. % (2 h) and 45.16 wt. % (3 h), respectively. The accumulated arabinose and galactose are depolymerized to furfural and 5-HMF with yield of 3.02 wt. % and 16.16 wt. %, respectively. With an increase in the dopant content in the catalyst, the total content of the products reaches 35.23 wt. % (5Al-5Zr-SBA-15) and 60.81 wt.% (10Al-5Zr-SBA-15) for 5 h, presumably due to the lower catalysts acidity.

Thus, the catalyst with an Al/Zr dopant ratio of 0.5 turned out to be the most active of the catalysts synthesized series and can be offered as a support for metals, (for example, Ru, Ni).

This work was supported by the Russian Science Foundation, Grant №21-73-20269.

References

1. Anwar Z., Gulfraz M., Journal of radiation research and applied sciences, 2014, 7 (2), 163–173.
2. Kelly G.S., Alternative medicine review: a journal of clinical therapeutic, 1999, 4 (2), 96–103.
3. Kusema B.T., et al., Catalysis letters, 2011, 141, 408–412.
4. Gromov V.N., Taran O.P., Parmon V.N., The Royal Society of Chemistry, 2018, 69–97.

Catalytic properties of silver nanoparticles immobilized in polymethacrylate matrix

S.K. Bragina

Tomsk State University, Tomsk, Russia

braginask@gmail.com

Natural enzymes, biological catalysts of protein nature, as a rule have high substrate specificity and catalytic efficiency, but their low stability, labor-intensive processes of isolation and purification as well as high cost limit their use for analytical purposes. In this connection, it is an important task to obtain artificial enzymes devoid of these disadvantages. Nanozymes, nanomaterials with inherent enzyme catalytic properties, have become a widely studied alternative to natural enzymes in recent years. Stability during storage, resistance to aggressive media, simplicity of preparation and low cost in combination with unique physical and chemical properties of nanomaterials, provide a variety of nanozymes applications, in particular in the development of analytical sensor systems.

Noble metal nanoparticles can serve as nanoenzymes (Ag, Au). Silver nanoparticles (Ag NPs) have a low cost, and their immobilization on solid substrates increases the stability of NPs and the storage time of nanozyme. The most studied enzyme-like activity of Ag NPs is peroxidase-like activity, because hydrogen peroxide is a product of many analytical reactions [1].

This work presents a nanocomposite based on silver nanoparticles immobilized in a polymethacrylate matrix (PMM-Ag^0) [2]. The nanocomposite demonstrates peroxidase-like activity in the reaction of hydrogen peroxide oxidation of various substrates, as well as serving as a chromogenic agent due to the presence of the surface plasmon resonance effect.

The peroxidase-like activity of PMM-Ag^0 was investigated by studying the catalytic oxidation reaction of a blue indigo carmine solution with an absorption maximum at 610 nm, forming a light yellow solution of isatin-5-sulfonic acid in the presence of H_2O_2. A model experiment was performed by taking absorption spectra of indigo carmine solutions ($C=2.3\cdot10^{-4}$ M, pH=4) upon the addition of different reagents 50 minutes after the start of the reaction. The solution containing PMM-Ag^0 sample without H_2O_2 ($C=2.7\cdot10^{-3}$ M) did not change color (remained blue). In the solution containing indigocarmine, hydrogen peroxide and the PMM-Ag^0 sample, there is no absorption peak at 610 nm, it has a light yellow color, this indicates that the oxidation reaction of indigocarmine to isatin-5-sulfonic acid was complete. Without adding PMM-Ag^0 to the solution, the oxidation reaction proceeds partially and the solution has a light blue color.

In order to obtain further insight into the catalytic behavior of PMM-Ag^0 nanocomposite, steady-state kinetic assays were carried out at the optimal conditions (pH 3.5 and temperature 50°C) by varying the concentration of H_2O_2 with a fixed concentration of indigo carmine, or varying the concentration of indigo carmine with fixed H_2O_2 concentration.

The kinetic parameters of catalytic activity were estimated by the initial rate method on the basis of the Michaelis–Menten equation, $V_0 = V_{max}[S]/(K_m+[S])$, where V_0, V_{max} and [S] represent the initial velocity of the reaction, the maximal rate of reaction and the substrate concentration, respectively. V_{max} and K_m are also calculated from the Lineweaver–Burk double-reciprocal plot. The absorbance signal was converted to concentration by the Beer–Lambert law ($A = \varepsilon bc$) where $\varepsilon = 8100\ M^{-1}cm^{-1}$ at 610 nm for the indigocarmine. The values of kinetic parameters determined by hydrogen peroxide were obtained: K_m = 0.97 mM; $V_{max} = 32.2\cdot10^{-8}\ M\cdot s^{-1}$. These data indicate a higher catalytic activity of the nanocomposite compared to the natural enzyme - peroxidase [3].

References

1. Cai S., Yang R., Nanozymology: Connecting Biology and Nanotechnology, 2020, 331–365.
2. Saranchina N.V., Bazhenova O.A., Bragina S.K., Semin V.O., Gavrilenko N.A., Volgina T.N., Gavrilenko M.A., Talanta, 2024, 126159.
3. Karim M.N., Anderson S.R., Singh S., Ramanathan R., Bansal V., Biosensors and Bioelectronics, 2018, 110, 8–15.

Phase composition and structural characteristics of $Ce_{1-x}Fe_xO_{2-\delta}$ ($0.25 \leq x \leq 0.75$) mixed oxides and silver catalysts on the basis thereof

S.N. Bukalova, M.V. Grabchenko, G.V. Mamontov

Tomsk State University, Tomsk, Russia

snbukalova237@gmail.com

There are many methods to purify the air from volatile organic compounds. One of the most effective methods is the use the catalysts containing noble metals. However, the use of such catalysts is limited due to their high cost [1]. Therefore, it is necessary to optimize the catalyst composition, e.g., by adding small amounts of noble metals [2]. Among the catalysts being studied, those based on CeO_2 are of interest due to their high oxygen mobility and intrinsic activity. Due to the fact that the redox potential of the $Fe^{3+/2+}$ pair is lower compared to $Ce^{4+/3+}$, the CeO_2 doped by Fe_2O_3 can become a mixed oxide support with higher oxygen capacity and can also be used as a catalyst for the total oxidation or reduction of VOCs in the presence of noble metal ions [3]. Therefore, the aim of this study is to investigate the effect of Fe_2O_3 addition to the CeO_2 matrix with varying the Ce/Fe ratio in $Ce_{1-x}Fe_xO_{2-\delta}$ ($0.25 \leq x \leq 0.75$) and the corresponding Ag-$Ce_{1-x}Fe_xO_{2-\delta}$ catalysts, to determine the phase composition, state, and distribution of the active Ag component in such catalysts.

The individual CeO_2 and Fe_2O_3 as well as mixed $Ce_{1-x}Fe_xO_{2-\delta}$ oxides with and without silver were obtained by co-precipitation method (constant silver loading of 5 wt%). The structural properties were investigated using XRD, while the textural properties were studied using low-temperature N_2 adsorption-desorption. The UV-Vis spectroscopy were used to determine the states of silver, iron oxide, and cerium oxide in the samples. HRTEM was used to study the sample morphology. Raman spectroscopy was used to study the structural features of the catalysts.

The XRD analysis was used to determine the formation of solid solutions based on the cubic CeO_2 phase in samples with different Ce/Fe molar ratios. An iron content increase in these samples leads to a decrease in the lattice parameter (a) of CeO_2 and an increase in microstrains ($\Delta d/d$) that can be explained by the Ce^{4+} substitution by Fe^{3+} in the ceria lattice and limitation of growth of crystallites in the mixed oxides (CSR is 7-9 nm). In the presence of silver, there is a higher decrease in lattice parameters. This can occur due to an increase in concentration of oxygen vacancies or the inclusion of Ag^+ ions in the crystal structure of $Ce_{1-x}Fe_xO_{2-\delta}$, as confirmed by the Raman spectroscopy and HAADF-STEM. The surface area of mixed oxides is generally higher than that of individual oxides, and the decrease in surface area for most Ag-containing samples can be attributed to interactions between silver, iron oxide, and ceria during synthesis. The UV-vis spectroscopy studies show that an increase in Fe content in $Ce_{1-x}Fe_xO_{2-\delta}$ features the increase in the Ce^{3+} fraction compared to Ce^{4+}. For Ag-containing systems, the surface plasmon resonance (SPR; a band at 420 nm) is clearly observed only in the Ag-CeO_2 sample. The HRTEM results show that silver is localized in the form of dispersed subnano-sized clusters and nanoparticles of 1-4 nm and in the form of single atoms which dope CeO_2.

This work was supported by the Russian Science Foundation, Grant № 23-73-10152.

References

1. Li K., Luo X., Catalysts, 2023, 13, 268.
2. Zhang L., Xue L., Lin B., Zhao Q., Wan S., Wang Y., Jia H., Xiong H., ChemSusShem, 2022, 15, 7.
3. Li B., Raj A., Croiset E., Wen J.Z., Catalysts, 2019, 9, 10, 815.

Bi-containing composite photocatalysts prepared by sol-gel method

R.A. Vergilessov, Y.A. Belik, O.V. Vodyankina

Tomsk State University, Tomsk, Russia

vergilesov.roman@bk.ru

Currently, various photocatalytic processes and systems are widely studied [1–3]. Photocatalysts are able to decompose many complex organic compounds at a significant rate even at low temperatures using the light energy. However, many photocatalytic possesses feature low activity in the visible range, which can be due to their wide band gap and a high probability of the charge carriers' recombination during the photocatalysis. It is possible to overcome these limitations by forming a composite structure. For instance, in a composite consisting of metasilicate and beta-bismuth oxide, a phase boundary is formed, due to which it is possible to reduce the energy of the band gap of semiconductors and recombination of charge carriers due to the spatial separation and concentration at different phases. This work is focused on the possible use of composite photocatalysts based on silicates and bismuth oxides. The aim of this work is to establish the influence of heat treatment conditions on the phase composition, structure and photocatalytic activity of the Bi-containing photocatalysts in the rhodamine B photodegradation reaction.

The studied photocatalysts were synthesized using the sol-gel method from the $Bi(NO_3)_3{\cdot}5H_2O$ and $Si(OC_2H_5)_4$ precursors followed by calcination at 400 (2 h) and 450 °C (4 h) to obtain the composite materials. Qualitative analysis of the phase composition of the samples was carried out using the X-ray diffraction (XRD), infrared (IR) and Raman spectroscopies. The optical properties were investigated using the UV-Vis diffuse reflectance spectroscopy. The photocatalytic activity of the prepared photocatalysts was evaluated in the rhodamine B photodegradation under irradiation with the light-emitting diodes (LEDs) with wavelengths of 375, 410, and 470 nm. The contribution of the active species (electronic vacancies h^+, hydroxyl radicals $OH^{\cdot}$, and superoxide radicals $O_2^{\cdot-}$) to the photocatalytic process was determined by measuring the rate of photodegradation of rhodamine B in the presence and absence of traps when irradiated with the 375-nm LEDs. To investigate the effect of superoxide radicals on the photodegradation of rhodamine B, the experiments were carried out using the prepared photocatalysts in the presence of benzoquinone, which acted as a trap for superoxide radicals. Additionally, the experiments were conducted by passing the air through a reactor in the presence of the synthesized photocatalysts.

The synthesized photocatalysts consist of α-, β-oxides of Bi_2O_3 and bismuth metasilicate Bi_2SiO_5. Based on the work done, we can draw the following conclusions: longer calcination at a temperature of 450 °C contributes to the formation of an interface between the metasilicate and β-bismuth oxide. Unlike calcination at 400 °C, this interface allows for the formation of a type II heterojunction, which spatially separates the photogenerated electrons and vacancies. This reduces their recombination and increases the quantum efficiency of the photocatalytic process. The formation of this interface plays a crucial role in photocatalysis as it affects the deethylation of rhodamine B under irradiation at a wavelength of 470 nm. We have shown that the electronic vacancies h^+ and hydroxyl radicals $OH^{\cdot}$ play a key role in the selective oxidation of rhodamine B. The superoxide radical $O_2^{\cdot-}$, on the other hand, participates only in the dye mineralization reaction.

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

References

1. Vodyankin A.A., Belik Yu.A., Zaikovskii V.I., Vodyankina O.V., JPPA: Chemistry, 2021, 408, 113091–113098.
2. Egorova L.S., Fakhrutdinova E., Svetlichnyi V.A., BRAS: Physics, 2022, 86, 1168–1173.
3. Reutova O.A., Fakhrutdinova E., Maliy L., Kharlamova T.S., Materials, 2022, 15, 7413.

Ag-containing catalysts for selective NO_x reduction

E.E. Eremina, E.S. L’vova, O.V. Vodyankina

Tomsk State University, Tomsk, Russia

blackcake1705@gmail.com

Currently, the atmospheric pollution with nitrogen oxides, which causes the formation of photochemical smog and the greenhouse effect, is an urgent issue [1]. One of the main sources of nitrogen oxides are diesel engines. A promising method to remove nitrogen oxides from diesel engine exhaust gases is the process of selective catalytic reduction of NO_x (SCR-NO_x). Catalysts based on CeO_2, MnO_x and silver as an active component attract attention not only for their activity in the SCR-NO_x process, but also for their relatively low costs compared to the catalysts used [2,3].

The aim of this work was to analyze the MnO_x effect in Ag/$CeMnO_x$ catalysts on the catalytic activity and selectivity in the process of the selective reduction of NO_x in the presence of CO.

The support samples comprising CeO_2, MnO_x and $CeMnO_x$ (Ce:Mn (mol.) = 1:1) were synthesized by the citrate sol-gel method. The Ag-containing catalysts (1 wt.% Ag) were obtained by wet impregnation with an aqueous solution of $[Ag(NH_3)_2]NO_3$. The phase composition was determined by the XRD analysis and Raman spectroscopy. The quantitative content of elements was determined using the XRF analysis. The morphology of the samples was studied using TEM. The reducing properties of the samples were studied using the temperature-programmed reduction in 10%vol. H_2 in Ar (H_2-TPR) and TPR-CO.

According to the XRD, it was shown that the formation of fluorite phase in the Ag/$CeMnO_x$ catalyst is observed. The Ag introduction into the MnO_x-based sample facilitates the appearance of the Mn_2O_3 phase. The Ag is uniformly distributed along the oxide surface in a nanodispersed state for all catalysts. According to the TEM results, the formation of a “patchwork” nanodomain structure in the Ag/$CeMnO_x$ sample is observed. The Ag interaction with the oxide supports was confirmed by Raman and TPR-CO data. During the catalytic studies, it was revealed that the Ag/CeO_2 and Ag/$CeMnO_x$ samples demonstrated high selectivity at low temperatures which was associated with the preservation of the activity of CeO_2, however, better thermal stability was observed for the Ag/$CeMnO_x$ sample due to the presence of MnO_x.

Thus, the uniform distribution of CeO_2 and MnO_x nanoparticles in the $CeMnO_x$ support helps to increase the activity of the Ag/$CeMnO_x$ sample in the SCR-NO_x process with CO addition due to the formation of the “patchwork” nanodomain structure, which allows maintaining the CeO_2 activity. The MnO_x addition to the Ag/$CeMnO_x$ catalyst helps to increase the NO conversion while the selectivity towards N_2 in the SCR-NO_x process with CO addition is kept at 100 % as a result of the mutual influence of MnO_x and CeO_2 that increases the thermal stability of the Ag/$CeMnO_x$ preventing sintering of the CeO_2 particles.

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

References

1. Wang L.K., Pereira N.C., Hung Y., Advanced air and noise pollution control, 2005, 537.
2. Salaev M.A., Kulchakovskaya E.V., Liotta L.F., Vodyankina O.V., Applied Catalysis A, Gen., 2022, 644, 118815.
3. Wu X., Liang Q., Weng D., Fan J., Ran R., Cat. Today, 2007, 126, 430–435.

Photocatalytic activity of bismuth silicate heterostructures $Bi_2SiO_5/Bi_{12}SiO_{20}$

A.G. Golubovskaya, V.A. Svetlichnyi

Tomsk State University, Tomsk, Russia

aleksandra.golubovskaya@mail.ru

Green technologies for environmental remediation have attracted significant interest recently. Such technologies include photocatalysis, one of the directions of which is the purification of water from organic compounds. Photocatalysis also has great potential for the recycling of renewable resources. The search for photocatalysts that are highly active in the decomposition of various organics (dyes, phenol derivatives, antibiotics) and in biomass processing, such as the selective oxidation of 5-hydroxymethylfurfural (5-HMF), is currently relevant. Excellent candidates for this role are bismuth-based semiconductor compounds [1], in particular bismuth silicates (Bi_2SiO_5 and $Bi_{12}SiO_{20}$). However, the rapid recombination of charges limits their efficiency. Modification of the band structure of semiconductor catalysts by creating heterojunctions of different types can solve this problem [2].

The approach proposed in [3], combining laser ablation and plasma laser treatment of colloidal solutions, was used to synthesize heterostructures based on bismuth silicates. To obtain $Bi_2SiO_5/Bi_{12}SiO_{20}$ heterostructures, colloidal solutions of Bi and Si were mixed in non-stoichiometric ratios of Bi:Si = 4:1 and 6:1. After drying the colloidal solutions in air (at 60°C), the powders were annealed at 500°C in a muffle furnace. Similarly obtained bismuth silicates in stoichiometric ratios of Bi:Si = 2:1 for Bi_2SiO_5 and Bi:Si = 12:1 for $Bi_{12}SiO_{20}$ were used for comparison. Characterization of the samples was carried out using XRD, FTIR and UV-Vis spectroscopy.

According to XRD data, the samples without laser treatment, in addition to the main phases Bi_2SiO_5 (60% for Bi:Si = 4:1 and 28% for Bi:Si = 6:1) and $Bi_{12}SiO_{20}$ (32% for Bi:Si = 4:1 and 67 % for Bi:Si = 6:1) also contain the β-Bi_2O_3 phase (8% for Bi:Si = 4:1 and 5% for Bi:Si = 6:1). After laser treatment, only two phases of bismuth silicates $Bi_2SiO_5/Bi_{12}SiO_{20}$ with component percentages of 53% / 47% (for Bi:Si = 4:1) and 72% / 28% (for Bi:Si = 6:1) are formed in the samples. Estimates of the band gap by the derivatives method (DASF) are consistent with the XRD data. For samples without laser treatment, the obtained band gap widths correspond to Bi_2SiO_5, $Bi_{12}SiO_{20}$ and β-Bi_2O_3 according to literature data. After laser treatment, two Eg values are obtained, which correspond to the bismuth silicates Bi_2SiO_5 and $Bi_{12}SiO_{20}$.

The photocatalytic activity (PCA) of the samples was investigated by the photodegradation of an aqueous solution of Rhodamine B under LED irradiation with λ=375 nm (radiation powers that were incident on the reactor of W=75 mW). The PCA of $Bi_2SiO_5/Bi_{12}SiO_{20}$ composite samples was found to be significantly higher than that of monophase samples. The samples after laser treatment showed the highest activity, with the reaction rate constant k = 0.1 min^{-1}. According to the calculation of the position of the energy bands, after laser treatment, a type II heterojunction of $Bi_2SiO_5/Bi_{12}SiO_{20}$ is formed in the samples, which leads to the efficient separation of electron-hole pairs and increases the activity of the samples. Samples without laser treatment show lower activity: k = 0.05 min^{-1} (for Bi:Si = 4:1) and k = 0.07 min^{-1} (for Bi:Si = 6:1). It is likely that the presence of the β-Bi_2O_3 phase slows down the process of charge separation and leads to a decrease in PCA.

Further studies will focus on testing the obtained materials in the reaction of selective photocatalytic oxidation of 5-HMF.

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

References

1. Li H., Cheng B., Zhang J., Zhou X., Shi C., Zeng L., Wang C., J. Environ. Chem. Eng., 2023, 11, 110371.
2. Emeline A.V., Rudakova A.V., Ryabchuk V.K., Serpone N., Curr. Opin. Green Sustain., 2022, 34, 100588.
3. Shabalina A.V., Fakhrutdinova E.D., Golubovskaya A.G., Kuzmin S.M., Koscheev S.V., Kulinich S.A., Svetlichnyi V.A., Vodyankina O.V., Appl. Surf. Sci., 2022, 572, 151732.

Study of selective photocatalytic oxidation of 5-HMF: search for optimal experimental conditions

V.E. Korepanov, O.A. Reutova, A.G. Golubovskaya, T.S. Kharlamova, V.A. Svetlichnyi

Tomsk State University, Tomsk, Russia

corepanow.vyacheslaw@yandex.ru

Increasing consumption of minerals can lead to a worsening of the energy and environmental crisis on the planet, in connection with this, attention is shifting to the use of renewable energy sources, one of which is biomass. Thus, from substances contained in biomass, 5-hydroxymethylfurfural (5-HMF) is obtained, the oxidation of which leads to the production of valuable intermediates: 2,5-diformylfuran (DFF), 5-hydroxymethylfurancarboxylic acid (HMFCA), 5-formylfurancarboxylic acid (FFCA), 2 ,5-furandicarboxylic acids (FDCA), which are promising intermediates in the synthesis of fungicides, drugs and polymers [1]. The most promising method for the oxidation of 5-HMF is photocatalysis, due to its environmental friendy, safety, carrying out the reaction under mild conditions at low temperatures, pressure and an accessible energy source - sunlight. Semiconductor oxides, composites, carbon nitride, etc. are considered as promising photocatalysts. One of the reference photocatalysts for the selective oxidation of 5-HMF is titanium dioxide TiO_2, due to its low cost, lack of toxicity, stability and catalytic activity. However, unlike heterogeneous catalysis, photocatalytic oxidation of 5-HMF does not achieve 100% selectivity for valuable intermediates. This is a problem that can be solved by selecting experimental conditions, as well as by modifying the photocatalyst. The purpose of the work is to study the influence of photocatalytic experimental conditions on the selective oxidation of 5-HMF in the presence of TiO_2.

Highly defective "dark" TiO_2 was obtained by pulsed laser ablation (PLA) of a VT1-0 Ti metal target in distilled water using a Nd:YAG laser with parameters: λ=1064 nm, τ=7 ns, ν=20 Hz by analogy with work [3]. The resulting colloidal solution of nanoparticles (NPs) was dried in air at 60°C, then calcined at 400°C.

Photocatalytic oxidation of 5-HMF was carried out in a quartz beaker under the soft UV LED irradiation with a wavelength of 375 nm, with the reactor air cooled to prevent thermal photocatalysis and stirred with a magnetic stirrer. One of the experimental conditions was to vary the pH of the medium by adding $NaHCO_3$, Na_2CO_3 and NaOH. The purging of the reaction medium (air, O_2, O_3, N_2, Ar) was also varied. At atmospheric pressure, the solution was purged with gas at a flow rate of 60 ml/min; when excess pressure was used, there was no purging. Photooxidation of 5-HMF was carried out for 8 hours. Samples were analyzed by HPLC.

It was found that varying the experimental conditions—changes in pH and oxygen saturation of the reaction mixture—allows one to change the depth of conversion, main products, and efficiency of 5-HMF photooxidation. The use of O_2 instead of air leads to a slight decrease in HMF conversion, but increases the selectivity of the oxidation process. The same result is achieved by creating excess gas pressure in the reaction system. Bubbling the reaction medium with O_3 results in the formation of FDCA, but the main product remains FFCA.

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

References

1. Ulyankina A., Mitchenko S., Smirnova N., Processes, 2020, 8, 6, 647.
2. Li C., Na Y., ChemPhotoChem., 2021, 5, 6, 502–511.
3. Fakhrutdinova E.D., et al., Materials., 2020, 13, 9, 2054.

Optimization of process conditions for tri-reforming coal mine methane into hydrogen-containing gas

E.V. Matus, E.N. Kovalenko, A.V. Salnikov, M.A. Kerzhentsev, S.R. Khairulin

Federal Research Center of Coal and Coal Chemistry SB RAS, Kemerovo, Russia

lizavetakovalenko@mail.ru

Activities associated with coal mining (underground mining, surface mining, and post-mining) are responsible for large amounts of CH_4 emissions into the atmosphere. Total methane emissions from the coal industry in 2022 amounted to 41.8 million tons, which is equal to almost 30% of anthropogenic methane emissions [1]. Emission factors for underground mining are 10 m^3/t – for mining depths of less than 200 m, 18 m^3/t – for depths from 200 to 400 m, 25 m^3/t – for mines with a depth of more than 400 m, and for surface mining by order of magnitude less: 0.3 m^3/t – for development depths less than 25 m, 1.2 m^3/t – for depths from 20 to 50 m, 2.0 m^3/t – for areas more than 50 m deep. Because the presence of methane in the atmosphere degrades air quality and contributes to global warming, efforts are being made to reduce methane emissions from coal mines [2]. One of the ways to utilize coal mine methane is its chemical processing using catalytic technologies.

Promising process for processing coal mine methane is the tri-reforming of methane (TRM: $3CH_4 + 0.5O_2 + H_2O + CO_2 = 4CO + 7H_2$). For TRM, the wet methane-air gas mixture from the mine's degassing system can use as is or by adding carbon dioxide to it. Thermodynamic analysis of this reaction showed that at 800 ºC the conversion of methane is 94%, the yield of hydrogen is 91%, and the concentration of hydrogen is 61% [3]. The aim of this work was to study the effect of temperature, contact time, linear feed rate and reaction mixture composition ($CH_4 : CO_2 : H_2O : O_2$: He) on the TRM process parameters and to determine the optimal reaction conditions for coal mine methane conversion into hydrogen-containing gas.

The $Ni/CeO_2/Al_2O_3$ catalyst was prepared by the citrate sol-gel method and contains 10 wt.% Ni and 6 wt.% Ce. The TRM was carried out in a flow quartz reactor (internal diameter 11 mm) at atmospheric pressure with varying temperature (600–850 ºC), contact time (0.04–0.15 s), linear feed rate (40–240 cm/min) and composition of the reaction mixture ($CH_4 : CO_2 : H_2O : O_2$: He = 1: (0.3–0.5) : (0.2–0.5) : (0.1–0.3) : (2.9–3.2)). It has been shown that with an increase in the temperature of the TRM reaction from 600 to 800 °C the process performance improves (methane conversion: 36→94%, carbon dioxide conversion: 57→97%, hydrogen yield: 37→91%, carbon monoxide yield: 44→94%, molar ratio H_2/CO: 1.5→1.7) and at a reaction temperature of 850 °C the process indicators are close to equilibrium values. The performance of the TRM process and the amount of carbon deposits depend on the molar ratio of O/C in the initial reaction mixture. It can be seen that the maximum yield of hydrogen with a small amount of carbon deposits is provided at an O/C molar ratio of 1.1–1.2. Lower values of this parameter lead to a sharp increase in coking, and higher values lead to an increase in the yield of the undesirable product – CO_2. To increase the resistance of catalysts to deactivation, it is necessary to purposefully regulate the O/C molar ratio in the initial reaction mixture by adding oxidizing reagents (H_2O, CO_2) to the coal mine methane. The optimum conditions of the TRM process for achieving maximum efficiency of catalytic conversion of coal mine methane into hydrogen-containing gas were determined: temperature - in the range of 800 – 850 °C, contact time – 0.15 s, linear feed rate – 160 cm/min and molar ratio of reactants in the feedstock – $CH_4 : CO_2 : H_2O : O_2 = 1 : 0.5 : 0.2 : 0.25$.

The investigation was carried out with support from the Russian Science Foundation under Project No. 22-13-20040, https://rscf.ru/project/ 22-13-20040/» and from the Region – the Kemerovo Region – Kuzbass.

References

1. Global Methane Tracker, 2023, IEA, https://www.iea.org/reports/global-methane-tracker-2023.
2. Driving Down Coal Mine Methane Emissions, IEA, https://iea.blob.core.windows.net/assets/ab2115cd-2b04-4e66-9a71-ec2c14d13acf/DrivingDownCoalMineMethaneEmissions.pdf.
3. Matus E.V., Ismagilov Z.R., Eurasian Chem. Technol. J., 2022, 24, 203–214.

Investigation of the peroxidase-like activity of silver and gold nanoparticles immobilized in a polymethacrylate matrix in the oxidation reaction of 3,3',5,5'-tetramethylbenzidine by H_2O_2

D.A. Kuznetsova, O.A. Bazhenova

Tomsk State University, Tomsk, Russia

dina.kuz.00@mail.ru

In recent years, considerable attention has been paid to the study of nanomaterials with enzyme-like properties – nanozymes. Compared to natural enzymes, nanozymes have several advantages, including resistance to harsh environments, low production cost, simple synthesis technologies, high stability, and ease of mass production. In the past few decades, noble metal nanoparticles have been extensively studied in catalysis due to many unique attributes. As promising candidates for natural enzymes, noble metal nanozymes demonstrated good tunability in activities and high stability. They were found to display multiple enzyme-like properties including oxidase-, peroxidase-, catalase-, and/or superoxide dismutase-like activities [1]. Nanomaterials can be immobilized on different solid surfaces that include polymers, cellulose, magnetic nanoparticles etc. The advantage of immobilization of noble metal nanoparticles on a solid support include uniform exposure of the particles to the reaction medium and allow removal of the particles from the reaction medium [2]. Noble metal nanoparticles with either positive or negative surface charges showed surprising peroxidase-mimicking activity. One of the widely used chromogenic substrates for hydrogen peroxide is 3,3',5,5'-tetramethylbenzidine (TMB). A key participant in the oxidation of 3,3',5,5'-tetramethylbenzidine is horseradish peroxidase (HRP), which serves as the catalyst. HRP is a natural enzyme, but its use in analytical procedures is limited due to storage difficulties, complex purification processes, high cost, and instability. Therefore, we propose using silver and gold nanoparticles immobilized in a polymethacrylate matrix (PMM) as catalysts for the oxidation of 3,3',5,5'-tetramethylbenzidine in the presence of hydrogen peroxide, as noble metal nanoparticles exhibit peroxidase-like activity, which is relevant.

PMM is a transparent polymer material containing carbonyl and carboxyl groups providing for solid-phase extraction and immobilization of analytical reagents thanks to the presence of hydrophilic fragments of polyethylene glycol 400 (PEG400) chain and polymethacrylate's robust hydrophobic polymer scaffolding (PMMA) in its structure. Noble metal nanoparticles are synthesized within small plates of pure polymethacrylate matrix by reducing metal cations. For this purpose, the PMM plates were placed into 10^{-3} M $AgNO_3$ or $HAuCl_4$ aquatic solution and stirred for 2–5 min. After that Ag(I) was reduced into PMM using thermal exposure in a thermostat at the temperature of 120–140°C for 2–5 min. The chemical reduction of Au (III) was performed by placing PMM-Au (III) plates into 1% $NaBH_4$ solution for 5 min. The samples of PMM with pre-adsorbed Ag(I) or Au (III) turned yellow or red with an absorption maximum of 420 nm or 530 nm respectively. The appearance of a surface plasmon resonance at 420 nm for Ag^0 and 530 nm for Au^0 indicated the formation of silver or gold nanoparticles with nanometer-sized dimensions in the PMM.

Pure 3,3',5,5'-tetramethylbenzidine (TMB) typically does not absorb in the visible spectrum. However, under the influence of hydrogen peroxide and in the presence of silver and gold nanoparticles immobilized in a polymethacrylate matrix, it can be oxidized to TMB^+, which appears blue (meriquinone complex). Subsequently, in an acidic medium, TMB^+ can convert to the final oxidation product TMB^{2+} , which is yellow (quinone diimine). Control experiments conducted in the absence of either noble metal nanoparticles or hydrogen peroxide did not show significant color changes in the system under similar reaction conditions, indicating that silver and gold nanoparticles exhibit peroxidase-like activity.

References

1. Yan X., Gao L., Nanozymology, Springer: Singapore, 2020, 564.
2. Alula M.T., Feke K. J., Clust. Sci., 2023, 34, 613–621.

Development of carriers based on γ-Al_2O_3 and ZSM-5 for Ni-Mo catalysts for the hydrotreating of waste cooking oil

D.I. Lashchenko[1,2], R.G. Kukushkin[2], K.S. Kovalevskaya[2], A.P. Lyulyukin[1, 2], V.A. Yakovlev[2]

[1]Novosibirsk State University, Novosibirsk, Russia
[2]Boreskov Institute of Catalysis, Novosibirsk, Russia

lashchenko@catalysis.ru

Climate change caused by human activities, including greenhouse gas emissions, is a significant problem attracting the attention of the scientific community. To reduce CO_2 emissions by the transport sector it is considered the use of biofuels due to its closed carbon cycle [1]. One of the promising types of feedstocks for the production of biofuels is waste cooking oil (WCO) which is a common and cheap waste of the food sector. A promising way to obtain biofuels from WCO is the process of its catalytic hydroprocessing, which includes the processes of hydrodeoxygenation (HDO) and hydroisomerization (HI), leading to the formation of high–quality fuel components - isomerized alkanes [2, 3]. However, an important task in the development of catalysts for the hydrotreatment of WCO and their subsequent industrial using is to maintain a balance between high catalytic activity and satisfactory mechanical strength.

In this work, a series of granules of composite carriers Al_2O_3-xZSM(y)-5 with different zeolite content and the value of the zeolite modules (x = 0, 10, 20, 30, 50, 60, 70, 95 – the mass fraction of zeolite at initial pseudoboehmite-zeolite powder mixture, y = 11.5, 15, 25 – the Si/Al ratio in ZSM-5). The preparation process included forming a paste of pseudobemite-zeolite, drying and heat treatment in an air atmosphere and, at the result, granular cylindrical extrudates were obtained. For all samples the values of radial strength during lateral crushing were determined. It was found that in each series, the strength depends non-linearly on the zeolite content, and the nature of the dependence changes along with the Si/Al ratio.

The maximum of strength is observed at 10-30 wt.% zeolite content, after which the strength began to decrease. The diffraction patterns of composite carriers show narrow reflexes from ZSM-5 and wide reflexes from Al_2O_3 which disappear with increase of zeolite content. The textural properties of the carriers were determined by the method of low-temperature adsorption-desorption of nitrogen. It has been demonstrated that for all samples an increase in the specific surface area and microporosity is observed with an increase of the zeolite content, while the average diameter of the mesopores has non-linearly dependance on composition. SEM and EDX mapping showed that in all samples of carriers zeolite is evenly distributed throughout the granule, however, with an increase in its content (more than 30-50 wt.%) there is a tendency towards the formation of larger ZSM-5 agglomerates The obtained extrudates were also characterized by TEM and IR-spectroscopy methods to explain the experimental dependance between mechanical strength and composition of samples.

For a quantitative study of the catalytic activity in the process of hydrotreating of WCO, nickel-molybdenum catalysts were prepared by impregnation according to moisture capacity on several carriers (4.6Ni-5.3Mo/Al_2O_3-xZSM(y)-5, x = 0, 10, 50, 95, y = 11.5, 15, 25) [4]. The obtained catalysts were characterized by physico-chemical methods. As a result of the experiments, it was demonstrated that the catalytic activity depends on the composition of the initial carrier, and the variation of the zeolite content, coupled with its Si/Al ratio, leads to a change in conversion, as well as the selectivity of the formation of isomerized alkanes and other products.

This work was supported by Ministry of Science and Higher Education (project no. FWUR-2024-0043).

References

1. Banga S., et al., J. Energy Nexus, 2023, 10, 100209.
2. Pham L.K.H., et al., Fuel Processing Technology, 2019, 185, 117–125.
3. Ameen M., et al., Renewable and Sustainable Energy Reviews, 2017, 80, 1072–1088.
4. Shinkevich K.S., et al., Applied Catalysis A: General, 2022, 644, 118801.

Alcohols as hydrogen donors in catalytic conversion processes of heteroatomic compounds of petroleum fractions

N.S. Nesterov, A.A. Philippov, A.A. Salomatina, O.V. Klimov, O.N. Martyanov

Boreskov Institute of Catalysis, Novosibirsk, Russia

nesterov@catalysis.ru

The development of effective technologies for deep processing of petroleum fractions remains one of the most important priorities of scientific and technological development of the chemical industry [1]. In addition to a high proportion of high-boiling hydrocarbons, heavy oil fractions contain a large number of organic heteroatomic compounds, including oxygen, sulfur, nitrogen, etc., which together dramatically reduce the efficiency of traditional catalytic oil refining technologies [2]. At present, catalytic hydrotreating processes using hydrogen gas are among the largest tonnage processes in the industry, but working with hydrogen gas is associated with a number of difficulties, such as explosion hazard and corrosion.

One of the most promising approaches for reducing transformations is the replacement of hydrogen gas with hydrogen donor compounds [3]. Lower alcohols can be very effective hydrogen donors due to their high hydrogen content and availability. We have previously shown that alcohols can effectively carry out the processes of deoxygenation and dearomatization of phenolic compounds using metal catalysts [4,5].

In this work, the H-donor potential of lower alcohols in the processes of reductive transformations of heteroatomic compounds of petroleum fractions containing oxygen, sulfur and nitrogen is studied. Ni-Mo-containing sulfide-deposited systems are used as catalysts. It is shown that the use of alcohols as hydrogen donors allows to effectively break the C-heteroatom bond, which opens prospects for the creation of new technologies for the processing of petroleum fractions.

This work was supported by the Russian Science Foundation, Grant 24-13-00208.

References

1. Marafi A., Albazzaz H., Rana M.S., Catal. Today, 2019, 329, 125–134.
2. Bello S.S., Wang C., Zhang M., Gao H., Han Z., Shi L., Su F., Xu G., Energy and Fuels, 2021, 35, 10998–11016.
3. Wang X., Rinaldi R., Energy Environ. Sci., 2012, 5, 8244.
4. Philippov A.A., Nesterov N.N., Pakharukova V.P., Martyanov O.N., Appl. Catal. A Gen., 2022, 643, 118792.
5. Nesterov N.S., Pakharukova V.P., Philippov A.A., Prosvirin I.P., Shalygin A.S., Martyanov O.N., Molecules, 2023, 28, 7041.

Ferrite nanoparticles $Fe_xCo_{3-x}O_4$ are active catalysts for the organic dyes degradation

O.S. Ivanova[1,2], I.S. Edelman[1,2], A.E. Sokolov[1,2], E.S. Svetlitsky[1], A.M. Popova[2]

[1]Kirensky Institute of Physics, Federal Research Center KSC SB RAS, Krasnoyarsk, Russia
[2]Siberian Federal University, Krasnoyarsk, Russia

osi@iph.krasn.ru

Co_3O_4 oxide is a semiconductor, an antiferromagnetic material with a spinel structure, one of the few compounds in which cobalt ions are in two charge states (Co^{2+} and Co^{3+}) and occupy two types of positions in the crystal - tetrahedral (A) and octahedral (B). The Co^{2+}/Co^{3+} sublattice distribution may differ from the distribution in normal 8/16 spinel and is determined by various external (magnetic field and temperature) and internal (particle size and slightly distorted CoO_6 octahedra) conditions. The replacement of some cobalt ions with ions of other metals causes strong changes in the magnetic and other properties. A special place is occupied by the compounds $Fe_xCo_{3-x}O_4$ [1-3]. Although ferrites have a suitable band gap for photocatalytic applications, their fast electron-hole relaxation time reduces their activity in photoreactions. The creation of mixed nanoparticles ferrites with different stoichiometry makes it possible to influence this process. Thus, the practical use of ferrite nanoparticles as catalysts in the decomposition reactions of organic pollutant molecules dissolved in water is an important area of modern science. The use of $Fe_xCo_{3-x}O_4$ nanoparticles as a catalyst is due to the formation of hydroxyl radicals (oxidizing agents) on their surface, promoting chemical oxidation/reduction of non-biodegradable organic pollutants, and their degradation to carbon dioxide, water and other substances, or transformation into harmless components, which is in demand method of water purification from organic dyes [4-7].

This work is devoted to the study of the photocatalytic properties of $Fe_xCo_{3-x}O_4$ nanoparticles, synthesized by the spontaneous combustion method using a citrate precursor and subjected to additional annealing at various temperatures for the degradation of organic dyes - Methylene blue (MB), Congo red (CR) and rhodamine (Rh), depending on duration of interaction, presence of oxidizing agent and interaction with UV radiation. The average crystallite size according to X-ray diffraction data varied from 5.2 to 48 nm when the additional annealing temperature varied from 400 to 800 °C for 1 hour. And the magnetization of nanoparticles increased non-monotonically with temperature, and at an annealing temperature of 700 °C, magnetic hysteresis appeared. In the sample without additional treatment and at processing temperatures from 400 to 600 °C, the magnetization is very low and its field dependences are close to super-paramagnetic. Of particular interest are the results of the degradation of the dyes MB and Rh, since these dyes tend to very easily reversibly transform into a colorless “leuco” form with subsequent regeneration of color and are difficult to decompose, for example, in comparison with the dyes CR and Methyl orange [8]. For catalysis experiments, nanoparticles were mixed with MB solution in the presence of oxalic acid $H_2C_2O_4$ (60 min at 30 °C in the dark). Next, the solutions in quartz cuvettes were subjected to UV irradiation, and the change in the optical density of the solution was recorded every 2 minutes. Within 10 minutes of UV irradiation, complete 100 % conversion of the MB dye occurred.

This work was supported by the Russian Science Foundation, Grant 23-22-10025, https://rscf.ru/project/23-22-10025/ and by the Krasnoyarsk Regional Science Foundation.

References

1. Kim K.J., Kim H.K., Park Y.R. et al., IEEE Transactions on Magnetics, 2005, 41, 3478–3480.
2. Omata K., Takada T., Kasahara S. et al., Applied Catalysis A: General 1996, 146, 255–267.
3. Li X., Wang Z., Zhang Bo, et al., Applied Catalysis B: Environmental 2016, 181, 788–799.
4. Zhang L., Wu Y., Journal of Nanomaterials, 2013, 640940.
5. Nazim S., Kousar T., Shahid M., et al., Ceramics International, 2016, 42, 7647–7654.
6. Yu J., Yu X., Huang B., Zhang X., Dai Y., Cryst. Growth Des. 2009, 9, 1474–1480.
7. Shabelskaya N.P., Egorova M.A., Arzumanova A.V., et al., Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol. [ChemChemTech], 2021, 64, 95–102.
8. Ivanova O.S., Lin, Chun-Rong, Edelman I.S., et al., Applied Surface Science, 2024, 665, 160236.

Photocatalytic properties of bismuth molybdate obtained by pulsed laser ablation in water

A.V. Volokitina, A.G. Golubovskaya, V.A. Svetlichnyi, T.S. Kharlamova

Tomsk State University, Tomsk, Russia

nvv0404@gmail.com

In the modern world, the use of photocatalytic processes is a promising and highly ecological direction. Photocatalytic technologies are relevant for hydrogen production [1], for clarification the environment from organic pollutants [2], for processing biomass intermediates such as 5-hydroxymethylfurfural (5-HMF) into valuable products [3]. Therefore, the development of efficient, inexpensive and safe semiconductor photocatalysts is a demanded issue of recent years. Bismuth-based catalysts have many useful qualities for photocatalytic processes [4]. However, many classical methods for their preparation require a large number of different precursors, complex sequential synthesis processes and careful additional purification from impurities. One of the promising methods for the preparation of complex semiconductor catalysts is the method of pulsed laser ablation (PLA) in liquid [5].

In this work, composite semiconductor photocatalysts based on bismuth molybdates (BMO) were prepared by PLA using the approach previously developed in [5]. For this purpose, colloidal solutions were sequentially synthesised by PLA of molybdenum and bismuth in distilled water using Nd:YAG laser 1064 nm (20 Hz, 7 ns, 150 mJ). After preparation, the colloids were mixed in different molar ratios of Bi:Mo as 1:1, 2:3 and 2:1. Part of the obtained colloids was subjected to additional irradiation with a focused laser beam (1064 nm,20 Hz, 7 ns, 150 mJ) for 3 hours. The irradiated and non-irradiated colloids were dried at 60ºC. Then the powders were annealed at 500ºC for 4 hours. The resulting samples are labelled BMO(1:1)-500, BMO(2:3)-500, BMO(2:1)-500, BMO(1:1)-hv-500, BMO(2:3)-hv-500, BMO(2:1)-hv-500.

X-ray diffraction analysis of the samples after annealing showed the formation of three main stoichiometric bismuth molybdate compounds in the samples: α-$Bi_2Mo_3O_{12}$, β-$Bi_2Mo_2O_9$ и γ-Bi_2MoO_6 in different ratios. Using diffuse reflectance spectra and derivative method (DASF), the forbidden band width of the samples was estimated and correlated with their composition. The photocatalytic performance was tested in the decomposition reaction of the model dye rhodamine B and selective oxidation of 5-HMF under 375 nm LED irradiation.

The dependence of photocatalytic activity of the samples on both the Bi:Mo ratio and the conditions of preparation, i.e., the use of additional laser treatment of colloids, was found. The obtained preliminary results showed the potential prospectivity of using composite samples of bismuth molybdates, BMO(1:1)-hv-500 samples showed high activity in the selective oxidation of 5-HMF, and for the photocatalytic decomposition of organic dyes – BMO(2:3)-500. Further studies will be directed to the establishment of regularities between the structure of catalysts and their properties and directed change of the phase ratio in composite catalysts in order to increase their photocatalytic activity.

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

References

1. Fakhrutdinova E., Reutova O., Maliy L., Kharlamova T., Vodyankina O., Svetlichnyi V., Materials, 2022, 15, 7413.
2. Vargas-Berrons K., Bernal-Jacome L., de Leon-Martinez L.D., Flores-Ramirez R., Sci. Total Environ., 2022, 726, 138493.
3. Golubovskaya A.G., Goncharova D.A., Fakhrutdinova E.D., Kharlamova T.S., Vodyankina O.V., Svetlichnyi V.A., Mater. Chem. 2024, 314, 128800.
4. Tian N., Hu C., Wang J., Zhang Y., Ma T., Huang H., Coord. Chem. Rev., 2022, 463, 214515.
5. Shabalina A.V., Fakhrutdinova E.D., Golubovskaya A.G., Kuzmin S.M., Koscheev S.V., Kulinich S.A., Svetlichnyi V.A., Vodyankina O.V., Appl. Surf. Sci., 2022, 575, 151722.

Influence of the nature of the modifying additive on the catalytic properties of γ-Al_2O_3 in the process of propane dehydrogenation

A.A. Vosmerikov, A.A. Stepanov, L.N. Vosmerikova

Institute of Petroleum Chemistry, Tomsk, Russia

antonvosmerikov@gmail.com

In recent decades, there has been a steady growth trend in global demand for light olefins, which is outpacing the rate of their production. Propylene is primarily produced as a by-product of petroleum refineries or steam crackers along with ethylene [1]. However, due to the rapidly growing demand for olefinic hydrocarbons, special production methods such as propane dehydrogenation are receiving increasing attention. Most often, the γ-modification of aluminum oxide is used as a catalyst carrier in this process. Commercially used catalysts consist of Al_2O_3 supported by Pt or CrO_x particles, which are responsible for the dehydrogenation of alkanes [2, 3]. However, commercial catalysts have disadvantages. The main disadvantage of platinum-based catalysts is their high cost; the main disadvantage of chromium (III) oxide-based catalysts is their rapid deactivation. Therefore, the development of new catalysts based on cheaper and more accessible promoters is an urgent task. The purpose of this work was to study the influence of the nature of the modifying additive (B, P, Mn, La) on the catalytic properties of γ-Al_2O_3 in the process of propane dehydrogenation.

The reaction of non-oxidative dehydrogenation of propane into propylene was carried out in a flow-type installation with a fixed bed of catalyst ($V = 3$ cm^3) in the temperature range of 550-650 °C and a volumetric feed rate of 500 h^{-1}. The reaction products were analyzed by GLC (Kristall 5000.2). The gamma form of aluminum oxide was obtained by heat treatment of pseudoboehmite (AlOOH) (Ishimbay Specialized Chemical Catalyst Plant LLC) at 550 °C for 4 hours. Modification of γ-Al_2O_3 was carried out by impregnating it with 4% B, P, Mn, La. Aqueous solutions of boric acid (H_3BO_3), ammonium phosphate ($(NH_4)_2HPO_4$), as well as manganese nitrate salts ($Mn(NO_3)_2 \cdot 6H_2O$) and lanthanum ($La(NO_3)_3 \cdot 6H_2O$) were used as promoter precursors.

The results of studies of the catalytic properties of the samples showed that modification of γ-Al_2O_3 with derivatives such as boron and phosphorus contributes to a slight decrease in their activity in the process of propane dehydrogenation. In this case, the selectivity of the formation of olefinic hydrocarbons increases. γ-Al_2O_3 modified with manganese has the greatest activity and selectivity with respect to the formation of olefin hydrocarbons from propane. The yield of olefin hydrocarbons on it is 25.3% already at a temperature of 600 ºC. Increasing the temperature to 650 ºC leads to an increase in yield to 34.8%. The sample modified with lanthanum differs slightly in overall activity from the sample prepared with manganese, but is somewhat inferior to it in dehydrogenating activity.

Thus, based on the results obtained, it was established that, taking into account all factors (activity, high selectivity for alkenes), the most effective among the studied modifying additives are manganese and lanthanum. The introduction of boron and phosphorus into the γ-Al_2O_3 composition leads to a decrease in activity and an increase in selectivity towards olefinic hydrocarbons compared to the original catalyst.

This work was supported by the Russian Science Foundation, Grant №24-23-00386.

References

1. Sokolov S., Stoyanova M., Rodemerck U., Linke D., Kondratenko E.V., J. Catal., 2012, 293, 67–75.
2. Vora B.V., Top. Catal., 2012, 55, 1297–1308.
3. Bricker J.C., Top. Catal., 2012, 55, 1309–1314.

Effect of Zr/Mn ratio in MnO_x-ZrO_2 catalysts for CO oxidation

E.E. Yashchenko, M.V. Grabchenko, M.A. Salaev

Tomsk State University, Tomsk, Russia

lensyashchenko13@gmail.com

The problem of air pollution by gaseous pollutants, including carbon monoxide and volatile organic compounds, is topical nowadays [1]. New effective solutions are required to this problem. Catalytic oxidation of such pollutants is one of the most effective ways of their utilization, and design of highly effective catalysts is required. Catalysts based on noble metals, such as Pd, Pt and Rh supported on oxide supports (CeO_2, Al_2O_3) are highly active materials in total oxidation reactions. Hopcalite is highly active in CO oxidation, while the material is rather sensitive to water vapor, rapidly deactivates, and is not exposed to regeneration. The catalysts based on transition metal oxides are more accessible and economically feasible alternatives to noble metals, which has a number of advantages, such as long service life, thermal stability, and resistance to catalytic poisons [2]. Among transition metal oxides, MnO_x occupies special attention due to its high activity as well as a number of unique chemical and physical properties. When ZrO_2 is added to MnO_x, an increase in catalytic activity is observed due to the interaction between oxides and the possibility of the formation of solid solutions [3]. Currently, the question of the ratio of active components Mn/Zr and the preparation method remains debating. Thus, the aim of this work is to study the influence of the Mn/Zr molar ratio on the structural and textural features of MnO_x-ZrO_2 oxide catalysts and their influence on the catalytic activity in CO oxidation.

A series of oxide catalysts based on ZrO_2, MnO_x and $Zr_{1-x}Mn_xO_{2-\delta}$ with the Zr/Mn molar ratios of 9, 4 and 2 were carried out by sol-gel method using citric acid as a complexing agent. The catalysts were characterized by XRF, XRD, low-temperature N_2 sorption, TPR-H_2, Raman spectroscopy and were tested in CO oxidation during 2 cycles.

The formation of the $Zr_{1-x}Mn_xO_{2-\delta}$ solid solution based on cubic phase of ZrO_2 at given molar ratios has been established. An increase in the molar content of Mn in a series of $Zr_{1-x}Mn_xO_{2-\delta}$ samples leads to an extreme decrease in the lattice parameter for cubic ZrO_2 phase and the value of microstrains at a comparable CSR size (7-8 nm), which can be due to the peculiarity of the interaction at Zr/Mn = 4 and/or due to subsequent limiting of the Mn dissolution in ZrO_2. It has been shown that the specific surface area of $Zr_{1-x}Mn_xO_{2-\delta}$ is higher than for individual manganese and zirconium oxides (3 m^2/g vs 70, 60 and 73 m^2/g, respectively), which can be a consequence of the formation of the solid solution. With an increase in the molar fraction of Mn in the structure of binary catalysts, an increase in catalytic activity in the CO oxidation reaction is observed. The increased catalytic activity of the $Zr_{0.8}Mn_{0.2}O_2$ sample in the low-temperature region (20% conversion is achieved at 128 °C) is explained by higher defectiveness (the lowest value of the lattice parameter and the value of microstrains).

This work was supported by the Russian Science Foundation, Grant No. 23-73-00109, https://rscf.ru/project/23-73-00109/.

References

1. Salaev M.A., Salaeva A.A., Kharlamova T.S., Mamontov G.V., Appl.Catal. B. Environ., 2021, 295, 120286.
2. Grabchenko M.V., Mikheeva N. N., Mamontov G.V., Cortés Corberán V., Litvintseva K.A., Svetlichnyi V.A., Vodyankina O.V., Salaev M.A. Nanomater., 2023, 13 (24), 3108.
3. Bulavchenko O.A., Konovalova V.P., Saraev A.A., Kremneva A.M., Rogov V.A., Gerasimov E.Yu., Afonasenko T.N., Catalysts, 2022, 13, 1, 57.

Features of Pt modification of dark titanium dioxide prepared via pulsed laser ablation to obtain highly efficient photocatalysts

E.V. Zinina, E.D. Fakhrutdinova

Tomsk State University, Tomsk, Russia

zinina_2000@list.ru

For photocatalytic hydrogen evolution reaction, the Pt/TiO_2 system is considered one of the most effective. Titanium dioxide is an active, photocorrosion-resistant, environmentally friendly semiconductor with a relatively low cost. However, TiO_2 has a low quantum efficiency and a limited spectral absorption region (λ <380 nm). Deposition of noble metals (Ag, Au, Pt) onto a semiconductor is often used as a method to increase photocatalytic activity. The use of noble metals as cocatalysts can provide an active site for the photocatalytic reduction/oxidation reaction, lead to increased absorption in the visible region, and also facilitate charge separation due to the formation of a Schottky barrier between the semiconductor and the metal [1]. The work examines the effect of various methods of depositing platinum on dark titanium dioxide, which has a high defectiveness, to increase the quantum efficiency of photocatalytic hydrogen evolution (HER). The work also assessed the effect of the influence of the platinum deposition medium to minimize the process of hydrolysis of the platinum complex, and also assessed the effect of the carrier (defective/non-defective TiO_2).

Platinum was loaded from the binuclear hydroxonitrate complex $(Me_4N)_2[Pt_2(OH)_2(NO_3)_8]$ (provided by the Institute of Inorganic Chemistry SB RAS, Novosibirsk) by three methods: by wet impregnation with followed by reduction in a flow of H_2/Ar; by chemical reduction method using an excess of the reducing agent $NaBH_4$; by photoreduction method using a fluorescent lamp with λ=280 nm. Defective dark TiO_2 was obtained by pulsed laser ablation in water. Titanium dioxide obtained by PLA in air was used as a reference sample (provided by the Institute of Electrophysics, Ural Branch of the RAS, Yekaterinburg). In all cases, the amount of platinum loading was 0.5 wt. %.

The Pt loading does not affect the phase composition of the samples; the anatase modification predominates in all materials. Diffuse reflectance spectroscopy studies have shown that Pt modification does not affect the edge of the TiO_2 absorption band. The dispersity (D, %) of platinum was determined by the method of pulsed CO adsorption, using acetone as a medium and the photoreduction method, the highest Pt dispersion value is achieved – 53%.

The study of the photocatalytic activity of the samples was assessed in the process of HER from an aqueous 20% solution of glycerol (sacrificial reagent) under LED irradiation with a wavelength of 375 nm. The sample obtained by wet impregnation method with subsequent reduction in a flow of H_2/Ar demonstrates the lowest apparent quantum yield AQY of 0.33, which correlates with the relatively low dispersion of Pt particles (37%). It was found that the samples using chemical and photoreduction as the methods of Pt loading show the highest photocatalytic activity; the calculated AQY of these samples are 0.77 and 0.78, respectively. The high activity of the samples is due to the high dispersion of Pt on the surface of dark TiO_2 and the appearance of the effect strong metal support interaction between Pt particles and the defective dark TiO_2 support.

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

References

1. Kumaravela V., Mathew S., Bartlett J., Pillai S.C., Applied Catalysis B: Environmental, 2019, 244, 1021–1064.

Enhanced photoelectrochemical activity of titanium dioxide nanotubes modified by Cu_xO for water splitting

N.A. Zos’ko[1], T.A. Kenova[1], A.S. Aleksandrovsky[2], O.P. Taran[1]

[1]*Institute of Chemistry and Chemical Technology, Krasnoyarsk, Russia*
[2]*L.V. Kirensky Institute of Physics, Krasnoyarsk, Russia*

rtkm.1@mail.ru

TiO_2 nanotubes produced by electrochemical anodizing of titanium foil are one of the most effective structures for the photocatalytic decomposition of water. However, the problems of high recombination rate of charge carriers and poor adsorption of visible light remain unsolved. Previously, various approaches to increase the sensitivity of titanium dioxide nanotubes to visible light have been reported, including the addition of metals or non-metals, sensitization to dyes, or modification of the surface with semiconductors with a smaller band gap [1,2]. However, little attention is paid to the modification of titanium dioxide with inexpensive, affordable materials that have great potential for their widespread use. One such material is Cu_xO, a p-type semiconductor with a band gap of about 2.2 eV. Thus, it can be used to form heterojunctions with broadband n-type semiconductors, which significantly increases the photoactivity of the latter when illuminated with visible light.

The paper presents the results of a comparison between the photoelectrocatalytic activity of pristine TiO_2 nanostructures and TiO_2 anode films modified by Cu_xO using either the CV (cyclic voltammetry) method or the potentiostatic method. In addition to Cu_xO, pre-activated TiO_2 films were also modified. [3].

The photoelectrocatalytic activity of the samples was studied in a water decomposition reaction by measuring the efficiency of converting incident photons into electrons (IPCE). This was done using chronoamperometry, which involves measuring current over time in a wide range of visible and ultraviolet spectra. When irradiated with visible light, IPCE of intact TiO_2 nanotubes remains extremely low, gradually increasing with decreasing wavelength. IPCE is 0.002% at a wavelength of 660 nm, 0.19% at 450 nm, and 6.2% at 370 nm.

The modification of TiO_2 with copper oxide increases IPCE when exposed to visible light and reduces it in ultraviolet. For CV-deposited Cu_xO, IPCE is 10-13 times higher (660-520 nm) while it is 2.5 times higher when irradiated with blue light (450 nm). Photoanodes modified by Cu_xO using the potentiostatic method demonstrated a 2-4 times lower photoactivity relative to the CV-deposited sample when irradiated with visible light.

The best IPCE results were demonstrated using pre-activated TiO_2 samples modified by Cu_xO. Their IPCE values in visible light is significantly higher than those for other studied samples and activated TiO_2 [3]. Depending on the applied method, the maximum IPCE values are 2.5% (450 nm) for the CV modification and 3.1% (520 nm) for the potentiostatically modified sample.

During the experiments, the modified Cu_xO photoanodes was found to have insufficient stability, which may be due to the electrochemical degradation of the deposited Cu_xO.

References

1. Ma T., Akiyama M., Abe E., Imai I., Nano Lett., 2005, 5, 2543.
2. Meekins B.H., Kamat P.V., ACS Nano, 2009, 3, 3437.
3. Zos’ko N.A., et al., ChemPhotoChem, 2023, 7, e202300100.

SECTION 3

PHYSICAL-CHEMICAL FUNDAMENTALS OF CATALYSIS

Detailing the mechanism of the SCR-CO reaction on Cu-OMS-2 catalysts by in-situ DRIFTS

E.D. Blinov, V.A. Svetlichniy, O.V. Vodyankina

Tomsk State University, Tomsk, Russia

egir.blinov@gmail.com

In recent years, a topical problem of environmental pollution, in particular atmospheric air, has become a consequence of the rapid development of industry. Today, air is one of the sources of toxicants for human such as volatile organic compounds (VOCs), CO, NO_x, soot particles, etc [1]. Promising catalysts for NO_x reduction in the presence of CO are systems based on MnO_2 with the OMS-2 structure due to their mixed valency of manganese and thermal stability [2]. The literature describes approaches to modifying the structure of OMS-2 by introducing various metals, including Ce or Fe, which are known for their easy redox transition [3]. It is also known from the literature that the introduction of Cu significantly improves the catalytic properties of OMS-2 in the SCR-CO reaction [4]. However, the mechanism of the SCR-CO reaction on Cu-containing catalysts based on OMS-2, modified with Ce and Fe has been not studied.

The purpose of this work is to detail the mechanisms of interaction of reagents - CO and/or NO - with the surface of copper-containing catalysts based on Ce or Fe-modified OMS-2 using in situ DRIFTS.

In this work, 2 series of Cu catalysts based on OMS-2 modified with cerium or iron ions were studied. Cu-containing catalysts were prepared by incipient impregnation method using a copper nitrate solution as a precursor. The synthesis of OMS-2 was carried out by co-precipitation from solutions of KMnO4 and $Mn(NO_3)_2$, followed by hydrothermal treatment at 120 °C for 24 h.

The physical-chemical properties of the obtained catalysts were studied by low-temperature nitrogen adsorption/desorption, XRF, XPD, Raman spectroscopy, TPR-CO, TEM, XPS. The catalytic activity of the obtained catalysts was studied in the SCR-CO process in a flow reactor with a stationary catalyst bed in the temperature range of 100-350 °C. The mechanism of interaction of NO and/or CO with the surface of the resulting catalysts was studied by in-situ DRIFTS using a “Praying mantis” cell (Harrick, USA) in the temperature range 100-350 °C.

Analysis of catalytical properties of the prepared Cu-containing catalysts showed that Ce-modified OMS-2 exhibited better catalytic activity in SCR-CO compared to the Cu/Fe-OMS-2 sample. Cu/Ce-OMS-2 showed 100% conversion of NO at 250 °C and 100% selectivity by N_2 at 300 °C. Cu/Fe-OMS-2 showed 100% conversion of NO at 200 °C and 100% selectivity by N_2 at 350 °C. Both of samples showed NO conversion even at 100 °C (26 and 30% for Cu/Ce-OMS-2 and Cu/Fe-OMS-2 respectively).

The report will discuss the influence of the modifying Fe/Ce cations in the OMS-2 support and the introduction of Cu into the catalysts on the activity and selectivity in the SCR-CO reaction, as well as on the mechanism of the reactions of the sequential conversion of NO into N_2O and N_2 and the simultaneous oxidation of CO into CO_2 on the surface of catalysts.

This work was supported by the Russian Science Foundation, Grant 19-73-30026P.

References

1. Levy R.J., Neurotoxicology and teratology, 2015, 49, 31–40.
2. Ni C., et al., Chemosphere, 2020, 250, 126211.
3. Kharlamova T.S., et. al, J. Alloys and Compounds, 2022, 917, 165504.
4. Li Y., et al., Applied Catalysis A: General, 2017, 530, 1–11.

XPS study of $[Ir(COD)Cl]_2$-L-SiO_2 single-site catalysts

K.G. Donskikh[1,2], L.M. Kovtunova[1,2], I.V. Skovpin[3], R.I. Kvon[2] A.V. Nartova[1,2]

[1]Novosibirsk State University, Novosibirsk, Russia
[2]Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
[3]International Tomography Center SB RAS, Novosibirsk, Russia

donskikh@catalysis.ru

Single-site catalysts combine the advantages of homogeneous and heterogeneous catalysts, which makes them promising for practice. The complex $[Ir(COD)Cl]_2$ (COD – 1,5 - cyclooctadiene) is used as the active component of a catalyst of this type with an active Ir^{1+} center. The complex is anchored to the surface of the oxide support through linkers containing functional groups. It is known that these complexes carry out the pairwise addition of molecular hydrogen to unsaturated hydrocarbons [1]. The effect of parahydrogen-induced polarization (PHIP) in nuclear magnetic resonance (NMR) is perfectly suitable for the investigation of the catalytic behavior of such catalysts [1].

The object of present research is $[Ir(COD)Cl]_2$ complex which is anchored to the porous SiO_2, the surface of which has been modified by linkers: $C_6H_{16}N_3$, C_7H_9N, $C_5H_{12}N$, C_3H_8N. The main purpose of the study is to determine the influence of the linker nature on the active component of the catalyst using the XPS. Based on the XPS analysis data, it was found that in all catalysts line Ir4f is represented by a state with a binding energy $E_b(Ir4f_{7/2})$ of 61.5 eV, which corresponds to Ir^{1+} [2]. Also, in all samples, except for the sample with the linker $C_6H_{16}N_3$, additional peaks in the Ir4f region with an binding energy $E_b(Ir4f_{7/2})$ of 61.7-61.9 eV were detected. According to the literature, the additional peak does not correspond to the new chemical state, but can be explained by the phenomenon of differential charging. Thus, it can be concluded that the preparation method used is suitable for anchoring the complex $[Ir(COD)Cl]_2$ on the SiO_2 surface. It has been experimentally shown that the complex $[Ir(COD)Cl]_2$ degrades under the influence of X-ray radiation [3]. The decomposition of the complex is seen by a decrease of chlorine recorded in the XPS spectra. Based on our experiment, conducted within 12 hours, it is shown that the Cl/Ir ratio remains at 1 for the first 5 minutes of X-ray exposure. Over the next 2 hours of the experiment, the chlorine content drops by 20%. To avoid a significant drop in chlorine during the experiment, it is required to start analyze the Cl2p region in the first 5 minutes of the experiment, giving it 2 scans of 0.5 seconds at a point. In this case, the Cl/Ir atomic ratio can be used as criterion of the complex stability both at the stage of sample preparation and after catalytic tests, carried out during the reaction of gas-phase hydrogenation of propene with parahydrogen in NMR spectrometer. Indeed, the Cl/Ir ratio also changes during catalytic tests. For example, for the catalyst with a linker C_3H_8N it was found that the Cl/Ir ratio is directly correlated with the enhancement of the NMR signal. The Cl/Ir ratio remains 0.93 when the signal is amplified to 78% at 60ºC and at 47% amplification at 80ºC. When the temperature rises to 100 °C, there is a sharp drop in signal gain, as well as the Cl/Ir ratio, which dropped to 0.38. These results indicate that at temperatures of 60°C and 80°C the catalyst is stable and at a temperature of 100°C it degraded.

The procedure of XPS experiments and analysis of XPS data used for the $[Ir(COD)Cl]_2$-L-SiO_2 catalysts is proposed. It is shown that used preparation procedure provides anchoring of the $[Ir(COD)Cl]_2$-complex through linkers over SiO_2. The temperatures of complex decomposition during the reaction of gas-phase hydrogenation of propene depending on the linker are estimated.

This work was supported by the the Ministry of Science and Higher Education of the Russian Federation within the framework of the state assignment of the Institute of Catalysis SB RAS (project FWUR-2024-0032), as well as the "Priority-2030" Program.

References

1. Nartova A.V. Kvon R.I. Kovtunova L.M. Skovpin I.V. Koptyug I.V. Bukhtiyarov V.I., Int. J. Mol. Sci., 2023, 24, 15643.
2. Moulder J.F., Stckle W.F., Sobol P.E., Bomben K.D, Eden Prairie, MN: Perkin-Elmer, 1992, 1–296.
3. Fernando N.K., Cairns A.B., Murray C.A., Thompson A.L., Dickerson J.L., Garman E.F., Ahmed N., Ratcliff L.E., Regoutz A.J., Phys. Chem. A, 2021, 125, 34, 7473–7488.

Optimal size of supported ruthenium nanoparticles for glucose hydrogenation

V.A. Golubkov[1], V.V. Sychev[1,2], V.A. Nasluzov[1], Y.N. Zaitseva[1], A.O. Eremina[1], O.P. Taran[1,2,3]

[1]*Institute of Chemistry and Chemical Technology SB RAS, Krasnoyarsk, Russia*
[2]*Institute of Non-Ferrous Metals, Siberian Federal University, Krasnoyarsk, Russia*
[3]*Boreskov Institute of Catalysis, Novosibirsk, Russia*

golubkov.va@icct.krasn.ru

Rational catalysts design appears to be a challenge in sorbitol production industry. The use of carbon materials as supports offers a number of advantages: hydrothermal and chemical stability, a wide range of textural characteristics, and usually low price. In addition, functional groups of various origin can be created on the surface of carbon materials, allowing one to tune the chemical properties of the support, and, consequently, the catalyst [1, 2].

A study was carried out to determine the effect of carbon support oxidative treatment on ruthenium particles dispersion. A series of supports based on carbon materials Sibunit-4 and CMK-3 were prepared. Supports surface modification aimed to create acidic surface species was employed via wet-air oxidation and sulfonation. Ruthenium catalysts were synthesized by incipient wetness impregnation method followed by reduction in a hydrogen flow. The supports and catalysts were characterized by nitrogen adsorption-desorption, XRD, XPS, TEM, acid-base titration, pHpzc determination.

The developed catalysts turned out to be highly efficient in the process of glucose hydrogenation providing a high selectivity (as high as 99%) towards sorbitol at a temperature as low as 60°C.

Using DFT modeling of a Ru cluster on graphene, the stabilization of smaller Ru particles in a presence of acidic surface species was demonstrated and particle size increase with excessive concentration of surface species was present. It was determined that hydroxyl and carboxyl species provide better stabilization of Ru particles than sulfonic ones. However, when a hydrogen atom transfer from the acidic species to the metal (reverse spillover) occurs, there is no deterioration in stabilization even with a high concentration of acidic species present.

The catalysts study by a set of physicochemical methods supported the results of DFT modeling. The oxidation and sulfonation leads to an increase in the surface species concentration and to a decrease in a size of the supported ruthenium nanoparticles. There is a tendency of the average Ru particle size decrease for both Sibunit (2.3 → 1.6 nm) and CMK-3 (1.6 → 0.9 nm) based catalysts series, when support modification is involved. The supports series with larger specific surface area (CMK-3) bears smaller Ru-particles. The carbon support oxidative treatment has opposing effect for Sibunit-4 and CMK-3 series in terms of catalytic activity. The Ru particle size on initial Sibunit-4 support is too big to provide the performance. For CMK-3 support the modification is unnecessary and only results in catalytic activity loss, since the initial particle size (around 1.6 nm) is found to be optimal.

To conclude, the oxidative treatment of carbon support makes it possible to tune the support properties and control the catalyst activity presumably in any hydrogenation reaction using molecular hydrogen. The developed ruthenium catalysts are characterized by a high atomic efficiency and proven to be stable. Their introduction into the sorbitol production will reduce the process cost in step of the product purification, thereby improving the environmental and economic indicators of plant raw materials valorization.

This work was supported by the Russian Science Foundation, Grant No. 21-73-20269, the equipment of the Center for Collective Use "National Center for Research of Catalysts" and the Krasnoyarsk Regional Center for Collective Use of the KSC SB RAS were used.

References

1. Taran O.P., Descorme C., Polyanskaya E.M., Ayusheev A.B., Besson M., Parmon, V.N., Catalysis in Industry, 2013, 5 (2), 164–174.
2. Toebes M.L., van Dillen J.A., de Jong K.P., Journal of Molecular Catalysis A: Chemical, 2001, 173, 75–98.

Insight into the mechanism of carbonyl compound isomerization into lactic acid over Ti^{4+}/Sn^{4+}-substituted UiO-66

A.V. Kotov[1], A.V. Fateev[1,2], O.V. Vodyankina[1]

[1]*Tomsk State University, Tomsk, Russia*
[2]*Tomsk State Pedagogical University, Tomsk, Russia*

asdfec01@yandex.ru

Analysis of mechanisms of liquid-phase catalytic reactions with identifying potential barriers and establishing the role of the catalytic sites is a non-trivial task. In many cases it is convenient to use cluster approach that allows constructing molecular models of any structural and impurity defects on the surface, models of surface functional groups, and describing the surface of amorphous solids. In the present work the reaction of isomerization of carbonyl compounds into lactic acid occurring over Lewis acid sites is studied. The metal-organic framework (MOF) UiO-66 possessing Lewis acid sites, i.e., uncompensated Zr^{4+} cations, was investigated as a catalyst in the dihydroxyacetone isomerization into lactic acid in water without alkali addition.

The geometries of reagents, intermediates, transition states, and the $Zr_{6-x}M_xO_4(OH)_4$ secondary building unit (SBU) with a single missing linker defect, where Zr/M = 1 ÷ 3, M = Sn, Ti, were proposed and optimized. The binding energy of the intermediate compounds and transition states in the carbonyl compounds isomerization into lactic acid over Zr^{4+}, Sn^{4+} and Ti^{4+} active sites as well as activation energies of transition states were estimated. The calculations were carried out using the Orca 5.0.3 software package at the B3LYP-D3/def2-tzvp level of theory [1] for O, C, H, Ti atoms and B3LYP-D3/SARC-ZORA-def2-tzvp level of theory [2] for Zr and Sn atoms to account for the relativistic interactions in the transition metals.

The IR vibrational frequencies for the CO molecules adsorbed on the active sites were calculated, and in situ IR spectroscopy was carried out to determine the geometric structure and distribution of substituent cations in the $Zr_{6-x}M_xO_4(OH)_4$ structure. The obtained theoretical and experimental data were compared with each other.

It has been shown that the doping of the UiO-66 secondary building unit with Sn^{4+} or Ti^{4+} cations increases the number of defects of the cluster, which leads to the growth of the amounts of active Lewis and Bronsted sites. The theoretically obtained data are confirmed by the experimental results of thermogravimetric analysis (TGA) and temperature-programmed desorption of ammonia (TPD-NH_3) for the prepared catalysts with the Sn-UiO-66 and Ti-UiO-66 composition.

It has been shown that the energy of binding of carbonyl intermediates on Sn^{4+}- and Ti^{4+}-containing active Lewis acid sites is by 3-15 kcal mol^{-1} lower than on those containing Zr^{4+}. The TOF was determined from the experimental data on the lactic acid yield, to evaluate the efficiency of catalysts based on substituted UiO-66. It has been shown that the introduction of 5 at.% substituent cations increases TOF, which is explained by a decrease in the adsorption energy of intermediates for substituted clusters, which is more preferably for the target reaction.

This report will also discuss the transition states of the pyruvaldehyde conversion into lactic acid on the SBU $Zr_{6-x}M_xO_4(OH)_4$, where Zr/M = 1 ÷ 3, M = Sn, Ti, which allows the intermediate to be converted into a product in one step due to the associative mechanism.

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

References

1. Weigend F., Ahlrichs R., Phys. Chem. Chem. Phys., 2005, 7, 3297–305.
2. Rolfes J.D., Neese F, Pantazis D.A, J. Comput. Chem., 2020, 41 (20), 1842–1849.

Influence of the B cation nature on the catalytic properties of copper-containing mixed oxides $CuBO_2$ (B = Mn, Ga, Co, Cr, Fe) with delafossite/crednerite structure

E.S. Kvasova, D.A. Svintsitskiy, V.M. Metalnikova, T.Yu. Kardash, A.I. Boronin

Boreskov Institute of Catalysis, Novosibirsk, Russia

es.kvasova@catalysis.ru

The search and development of novel, cheap and highly efficient catalytic systems is an urgent task for the scientific community as part of solving modern challenges in the development of industry and technology. Promising objects in the field of oxidative catalysis are mixed oxides of the composition $CuBO_2$ (B — trivalent transition metal) with a delafossite/crednerite type structure [1,2]. The variation of the preparation conditions as well as the choice of B cation makes it possible to obtain $CuBO_2$ oxides with tunable reaction and catalytic properties in comparison with individual oxides [3,4]. It is due to the presence of metals with variable valence providing the possibility of additional redox transitions between Cu^{2+}/Cu^{1+} and $B^{n+}/B^{(n+1)+}$ electronic pairs with the preservation of mixed oxide structure. The aim of this work is to synthesize and compare the catalytic properties of $CuBO_2$ double mixed oxides in the reaction of CO oxidation in dependence of the nature of B cation (Mn, Co, Cr, Ga, Fe) with different ability to change valence under reaction conditions.

The phase composition was determined using XRD method. The surface state and surface composition of both the initial samples and the samples after catalytic measurements were studied using the XPS method. Thermal stability was studied by the TGA method when heated in helium or in air. TPR-CO study revealed an oxygen mobility and oxygen reactivity. The catalytic tests were carried out in a flow-through reactor in model reaction of CO oxidation under dry and wet conditions. Methods for the synthesis of double oxides $CuCoO_2$, $CuCrO_2$, $CuFeO_2$ and $CuGaO_2$ with a delafossite- type structure using hydrothermal and glycine-nitrate approaches have been developed, while the preparation conditions for $CuMnO_2$ crednerite was previously established [5]. A combination of Co2+/Co3+ forms was observed on the initial surface of $CuCoO_2$. The states of chromium and gallium or iron on the surface of the $CuCrO_2$, $CuGaO_2$ and $CuFeO_2$ oxides were close to 3+. Copper was present on the surface of all the studied catalysts in the combination of Cu^{1+} and Cu^{2+} forms with the predominant contribution of first one. The influence of the nature of B cation on the copper state is discussed.

All mixed oxides were pretreated in a catalytic mixture of $CO+O_2$ at 250–300 °C and 350–550 °C, resulting in the preservation of initial structure or its transformation into spinel-like particles respectively. Among the samples with the initial delafossite/crednerite type structure, the most active catalysts in the low-temperature region were the $CuCoO_2$ and $CuMnO_2$ samples, for which the specific rate of CO oxidation (W_{35}) in dry oxidation was close to ~2·1015 molecules/(m^2·s), which is ~1.5 times higher than for delafossite $CuCrO_2$, while $CuGaO_2$ and $CuFeO_2$ exhibited an order of magnitude lower catalytic activity. Under wet conditions, all samples were significantly deactivated without showing noticeable catalytic activity below 70 °C, that was accompanied by the growth of apparent activation energy up-to 73 kJ/mole. Pretreatment at elevated temperatures resulting in the formation of spinel-like $Cu_xB_{3-x}O_4$ particles led to catalytic activation in both dry and wet oxidation. The low-temperature catalytic activity of studied Cu-containing mixed oxide was discussed in correlation with the presence of highly reactive oxygen species on the surface in accordance with TPR-CO data. Enhanced catalytic activity of Cu-Mn and Cu-Co mixed oxides is probably relates to the labile electronic transitions between copper/manganese and copper/cobalt species respectively as confirmed by XPS data.

This work was supported by the Russian Science Foundation, Grant No. 23-73-10127 dated 14.08.2023.

References

1. Dey S., et al., Bulletin of Chemical Reaction Engineering & Catalysis, 2017, 12, 437–451.
2. Huang R.J., et al., RSC Advances, 2021, 11, 12607–12613.
3. Christopher J., Swamy C.S., Journal of Materials Science, 1992, 27, 1353–1356.
4. Xu C., et al. Separation and Purification Technology, 2022, 291, 120933.
5. Sokovikov N.A., et al., Journal of Structural Chemistry, 2023, 64, 1098–1113.

A comparison of mixed oxides $AgFeO_2$ and $AgMnO_2$: the role of silver surface state in low-temperature catalytic CO oxidation

V.M. Metalnikova, D.A. Svintsitskiy, S.V. Cherepanova, A.I. Boronin

Boreskov Institute of Catalysis, Novosibirsk, Russia

v.metalnikova@g.nsu.ru

Catalysts based on transition metal mixed oxides are widely used in the industrially and environmentally important process of CO oxidation [1] due to the ability to modify the properties of active oxygen by selecting metals as well as varying synthesis and post-treatment conditions. Mixed oxides with a delafossite-type structure are promising materials in the field of oxidative catalysis. Such oxides are described by the formula ABO_2 (A=Ag, Cu; B=Ni, Mn, Fe, etc.) and characterized by the presence of low-coordinated A-centers available for adsorption, a developed defective structure, the formation of interface species as a result of partial or complete decomposition of the initial structure [2]. It is predictable that the nature of the B cation affects the A cation state, which is obvious in the case of labile copper-containing $CuBO_2$, but is almost not discussed for silver-containing systems. A comparative study of $AgFeO_2$ and $AgMnO_2$ was conducted in order to investigate correlation between the nature of the B cation, silver state and catalytic activity in low-temperature CO oxidation and to establish the influence of the reaction mixture on the bulk and surface structure of $AgBO_2$ at the temperatures 25ºC-600ºC.

Mixed oxides $AgBO_2$ (B=Fe, Mn) were obtained with help of hydrothermal synthesis in an alkaline medium. According to the XRD data, the structure of $AgFeO_2$ and $AgMnO_2$ particles was characterized by a high density of stacking faults - microtwins. The CO oxidation activity was enhanced in the case of $AgMnO_2$ in comparison to $AgFeO_2$, however treatment at 350 and 450°C in the reaction media led to the decrease in the low-temperature activity of $AgMnO_2$. At the same time, oxidative activity of the $AgFeO_2$ was not affected by high-temperature treatment. The influence of reaction mixture on the mixed oxide structure and the surface state was studied by using TGA, TPR-CO, *ex situ* ($CO+O_2$) XPS and *in situ* ($CO+O_2$) XRD.

From the TGA and *in situ* XRD data it was found that both $AgFeO_2$ and $AgMnO_2$ particles are stable in O_2-containing media up to 500°C. Above 600°C, mixed oxides were destroyed with the formation of Ag^0 particles and Fe_2O_3 or Mn_3O_4, correspondingly. However, during the *in situ* ($CO+O_2$) XRD study of the $AgMnO_2$ the appearance of metallic silver (~0.8 wt.%) was noted in the range of 100-150°C, the amount of which decreased with increasing temperature until it completely disappeared at 300°C. During the TPR-CO experiments the reduction of mixed oxides $AgFeO_2$ and $AgMnO_2$ occurred in two stages with maximum of CO_2 release at 266 and 481°C in the case of $AgFeO_2$ and at 246 and 291°C in the case of $AgMnO_2$. It should be noted that for $AgMnO_2$ interaction with CO was also observed in the range of 25-150°C, which is due to the presence of reactive oxygen on the surface of the particles.

The surface state and composition were determined by using the *ex situ* XPS. For the initial surface of mixed oxides, the main state of silver was Ag^{1+} with signs of the presence of a highly oxidized form Ag^{2+}, the contribution of which in the case of $AgMnO_2$ was noticeably higher than on the surface of $AgFeO_2$. During the interaction of mixed oxides with a catalytic mixture in the range of 25-200°C, the oxidized states of Ag^{1+} and Fe^{3+}/Mn^{3+} were preserved, and the contribution of Ag^{2+} forms decreased. For $AgFeO_2$ at the $T>250°C$ there were signs of surface modification by the formation of amorphous forms of FeO_x. In the case of $AgMnO_2$, signs of $Mn^{3+} \rightarrow Mn^{4+}$ oxidation were noted at $T>300°C$. Taking into account coexistence of Ag^{1+}, Ag^{2+} and Ag^0 species on the surface of activated $AgMnO_2$ oxide as well as the high reactivity of Ag^{2+} towards CO oxidation at $T \leq 100°C$, the enhanced redox lability of silver surface species is assumed for $AgMnO_2$ under the reaction conditions in contrast to $AgFeO_2$.

This work was supported by the Russian Science Foundation, Grant 23-73-10127.

References

1. Sokovikov N.A., Svintsitskiy D.A., Cherepanova S.V., Boronin A.I., Surfaces and Interfaces, 2024, 45, 103887.
2. Marquardt M.A., Ashmore N.A., Cann D.P., Thin Solid Films, 2006, 496, 146–156

Delafossite-type Ag_2CuMnO_4 catalyst for low-temperature CO oxidation

N.A. Sokovikov, D.A. Svintsitskiy, E.M. Slavinskaya, S.V. Cherepanova, A.I. Boronin

Boreskov Institute of Catalysis, Novosibirsk, Russia

sokovikov@catalysis.ru

Carbon monoxide oxidation has drawn considerable attention due to its importance in application, especially, respiratory protection. Transition metals oxides (for instance, copper + manganese as part of “hopcalite”) are still favored for commercial application due to their efficiency and low cost. Even though low-temperature CO oxidation has been widely studied, the mechanism of this process on oxide materials still remains under discussion [1]. This work aims to establish structure-activity relationship for Ag_2CuMnO_4 oxide exhibiting high activity at sub-ambient temperatures through in-depth surface and bulk structure analysis.

An original procedure of hydrothermal synthesis was used for a preparation of the ternary oxide Ag_2CuMnO_4. This method requires the use of widely available commercial reagents. X-ray diffraction pattern for synthesized material corresponds to crystal delafossite-type phase of Ag_2CuMnO_4 without any impurities. XPS results established the presence of Ag^+, Cu^{2+} and predominantly Mn^{4+} charge states on the oxide 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 $5\cdot10^{-7}$ $mol\cdot g^{-1}\cdot s^{-1}$ and activation energy was equal to 25 kJ/mol. In contrast to $CO+O_2$ reaction mixture the interaction of Ag_2CuMnO_4 with CO/He reaction mixture (without O_2) resulted in the evident deactivation of delafossite. Hence, room-temperature CO oxidation over Ag_2CuMnO_4 can be referred to the catalytic type of reaction. 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 proceed catalytic oxidation of carbon monoxide for more than 5 hours unlike the commercial hopcalite catalyst.

Also we studied the influence of heating pretreatments in different gas atmospheres on catalytic activity in the connection with surface and bulk properties analyzed with the use of XPS *ex situ* and XRD *in situ* techniques. *Ex situ* XPS data proved the realization of Cu-Mn charge transfer within the delafossite Ag_2CuMnO_4 structure in the presence of CO at low temperatures. The most active state of the ternary oxide was found to occur after the heating in the inert or reaction ($CO+O_2$) atmosphere at 250°C. The pretreatment led to 10-fold increase in CO oxidation rate. This state was correlated with the interlayer charge transfer through the Cu^+ and Ag^+ ions in the linear coordinated position within the delafossite structure. The heating above 300°C caused the accumulation of tetrahedral Cu^+ cations as part of the “proto-spinel” entities leading to the drop of catalytic activity. The appearance of “proto-spinel” facilitates the obstruction of octahedral layer pattern limiting the charge transfer along the polyhedral layer.

Thus, ternary oxide Ag_2CuMnO_4 is highly promising catalytic material in terms of low-temperature oxidation activity. The oxide Ag_2CuMnO_4 can be considered as novel catalytic system for prolonged CO oxidation under ambient conditions (high humidity, room temperature). The catalytic characteristics of Ag_2CuMnO_4 delafossite can be improved via pretreatments in different gas media. The low-temperature activity proved to be linked with the preservation of bulk delafossite structure, the compliance with octahedral layer geometry and the emergence of charge transfer between the octahedral layers through the linear cations.

This work was supported by the Russian Science Foundation, Grant 23-73-10127.

References

1. Wang J., Chen J., Peng L., Zhang H., Jiang Z., Xiong K., Yang Q., Chen J., Yang N., Appl. Surf. Sci., 2022, 575.

Formation of active sites in Mo- and NiMo-catalysts for light alkenes conversion by *ex situ* EPR spectroscopy

V.L. Yurpalov, T.R. Karpova, A.V. Lavrenov, M.A. Moiseenko

Center of New Chemical Technologies BIC, Boreskov Institute of Catalysis, Omsk, Russia

yurpalovv@mail.ru

The study of oxygen-surrounded transition metal ions in paramagnetic form, for example, Mo^{5+} cations of supported molybdates is of interest for the development of catalysts [1], in particular, for the metathesis of alkenes [2]. Many researchers made a lot of attempts to determine the role of paramagnetic Mo^{5+} species in metathesis reactions by EPR in order to clarify the nature and structure of active sites [3–7]. The ambiguity and inconsistency of the information obtained leaves opportunity for studying the problem by the new approaches. In current work, an *ex situ* EPR methodology was used for the first time to study supported molybdenum oxide and nickel molybdenum oxide catalysts under the reaction conditions (ethylene or propylene reagent contact).

A series of MoO_3/Al_2O_3 (MoA) and NiMo/support catalysts were studied (where supports are γ-Al_2O_3 (A), SiO_2 (Si), B_2O_3-Al_2O_3 (BA), SO_4^{2-}-Al_2O_3 (SA) and SO_4^{2-}-ZrO_2 (SZ)) [8, 9]. The content of molybdenum oxide varied from 2 to 10% wt. *Ex situ* EPR-spectra were recorded at 25°C for the samples after propylene (for MoA samples) or ethylene (for NiMo/support samples) treatment at 200°C in an activation cell. Theoretical EPR-spectra of Mo^{5+} in tetrahedral and octahedral coordination were obtained based on literature data [3, 4].

As a result of *ex situ* EPR-experiments for MoA catalysts of propylene metathesis the presence and concentration of surface molybdate clusters (Mo^{5+}) signals were determined. It has been found that the activity of catalysts in the propylene metathesis reaction is directly proportional to the increase in the concentration of Mo^{5+}paramagnetic species, determined after the contact with propylene under the reaction conditions. In the series of studied supported NiMo catalysts for the most samples a partial reduction of Mo^{6+} to Mo^{5+} occurs after activation, which is characterized by the increase of EPR signal intensity. The spectra obtained after the treatment of the catalysts with ethylene for the most (NiMo/BA) and least (NiMo/SZ) active samples in the reaction differ significantly due to the different contributions of paramagnetic Mo^{5+} species in octahedral and tetrahedral coordination to the overall EPR signal. In all the catalysts, except NiMo/SZ, EPR signals of tetrahedral molybdenum are presented and its proportion in alumina-based samples (NiMo/A, NiMo/BA, NiMo/SA) significantly exceeds the proportion of octahedral Mo^{5+}, while in NiMo/Si sample molybdenum is presented only in the octahedral coordination. The symmetry of the curves of changes in the tetrahedral molybdenum amount in a series of samples and their catalytic activity suggests that tetrahedral Mo^{5+} species may be an active site of the reaction or may be the part of an active paramagnetic complex with an alkene molecule.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the governmental assignment for Boreskov lnstitute of Catalysis (project FWUR-2024-0039).

References

1. Dyrek K., Che M., Chem. Rev., 1997, 97, 305–331.
2. Brenner A., Burwell R.L., J. Catal., 1977, 52, 367–374.
3. Zhaug B., et al., J. Mol. Catal., 1991, 65, 15–28.
4. Grunert W., et al., J. Catal., 1992, 135, 269–286.
5. Handzlik J., et al., J. Mol. Catal. A., 2000, 157, 237–243.
6. Nikolova D., et al., Appl. Catal. A., 2006, 297, 135–144.
7. Zhang D., et al., Appl. Catal. A., 2014, 472, 92–100.
8. Yurpalov V.L., et al., AIP Conf. Proc., 2020, 2301, 040020 (1–4).
9. Karpova T.R., et al., Catal. Ind., 2021, 13, 352–360.

The effect of acid catalysts on kinetic parameters of condensation of glyoxalic acid with urea

P.K. Krivolapenko, V.P. Tuguldurova

Tomsk State University, Tomsk, Russia

kpk36@mail.ru

There is the first mention about allantoin medicinal properties in the ref. [1], followed by a series of discoveries proving its medical importance. Antimicrobic, antioxidant properties, and high biocompatibility [2] provide allantoin a wide application sphere in pharmacy, cosmetology and veterinary medicine. Also, participation in the purine catabolic pathway makes for its using in agriculture as a fertiliser.

Allantoin is a typical substance of imidazolidinone compounds. These compounds were used for obtaining supramolecular compounds, which can be application as container molecules [3]. However, the first step for understanding the mechanism of complex molecules formation is the study of the mechanism and kinetic regularities of simple molecules formation.

The reaction for the synthesis of allantoin was chosen as an example. Condensation of glyoxalic acid and urea in the presence of mineral acids [4] is the simplest reaction for its synthesis. Thus, the aim of the work was analyzed the dependence between mineral acid strength and kinetic parameters of the reaction.

Urea consumption kinetic curves in the reaction were obtained on an iHR SP320 CR spectrometer (Horiba Scientific, Japan) with an immersion probe [5] in the *in situ* mode. The reaction order was determined from these kinetic curves, and the rate constants and activation energies were calculated accordingly. Kinetic curves comparison for the same temperature with different catalysts showed the dependence of kinetic parameters on the acid catalyst strength: with increasing acid catalyst strength, the reaction rate increases and the activation energy decreases.

The research was supported by the development program of Tomsk State University (Priority-2030).

References

1. Robinson W., JBJS, 1935, 17, 267–271.
2. Araújo L.U., Grabe-Guimarães A., Mosqueira V C.F., et al., Acta Cirurgica Brasileira, 2010, 25, 460–461.
3. Svec J., Necas M., Sindelar V., Ang. Chem. Int. Ed., 2010, 49, 2378.
4. Hu W., Pan Yo., C.N. Patent 102 617 476, Method for synthesizing allantoin, 2012.
5. Marquardt B.J., Burgess L.W., U.S. Patent 6977729 B2, Optical immersion probe incorporating a spherical lens, 2005.

The influence of potassium on the catalytic properties of platinum-titanium catalysts for the selective oxidation of ammonia

I.Yu. Ovsyuk[1,2], L.S. Kibis[2], D.A. Svintsitskiy[2], O.A. Stonkus[2], T.Yu. Kardash[2], A.V. Romanenko[2]

[1]*Novosibirsk State University, Russia*
[2]*Boreskov Institute of Catalysis, Novosibirsk, Russia*

i.ovsyuk@g.nsu.ru

Ammonia is an important product of the chemical industry; however, it is also a toxic gas that is present in the exhaust of diesel vehicles and thermal power plants [1]. For environmental safety, ammonia must be oxidized to molecular nitrogen. Pt-based catalysts are often used for this purpose [2]. They exhibit activity at low temperatures (below 250°C), but have relatively low selectivity towards molecular nitrogen (70-80%) [3]. In this regard, fundamental studies of the key factors determining the selectivity of low-temperature oxidation of ammonia on platinum-containing catalysts still remain relevant. In this work, the catalytic and physicochemical properties of a series of platinum-titanium catalysts modified with potassium were investigated.

The basic platinum-titanium (Pt/TiO_2) sample contained 2 wt.% of Pt deposited on titanium dioxide (Aeroxide, P25, Degussa) from a platinum nitrate solution by incipient wetness impregnation. Potassium-containing samples (0.5 wt.% of potassium) were prepared by impregnation of the Pt/TiO_2 sample with KOH, KNO_3 or KCl solutions. Also, part of each catalyst was reduced in a stream of hydrogen at 250°C. The activity of the samples in the ammonia oxidation reaction and selectivity towards molecular nitrogen were determined during the temperature-programmed reaction NH_3+O_2 (TPR NH_3+O_2) in a flow reactor. To study the phase composition of the samples, the X-ray powder diffraction method was used. The surface composition of the catalysts and the charge states of the elements on the surface were characterized by XPS.

According to TPR-NH_3+O_2 data, the Pt/TiO_2 catalyst and samples modified with KOH and KNO_3 demonstrate similar activity: NH_3 conversion is observed at temperatures above 180°C (T_{50}~200°C). Modification of the Pt/TiO_2 sample with potassium chloride promotes the appearance of activity in the ammonia oxidation reaction already at a temperature of 150°C (T_{50}~180°C). In the catalytic experiment, almost all reduced catalysts demonstrated a lower value of the 50% NH_3 conversion temperature (T_{50}~180°C) compared to the initial catalysts (T_{50}~200°C). Only the activity of the KCl-based catalyst was not influenced by the reduction pretreatment. Below 200°C most of the catalysts achieved nitrogen selectivity up to 80%, while the selectivity of the samples prepared from potassium chloride reached 90%.

The results of XPS studies showed the presence of three forms of platinum in all samples with Pt $4f_{7/2}$ binding energy values: 70.9, 72.5-72.6 and 74.1-74.3 eV. These platinum species correspond to platinum in the oxidation states 0, 2+, and 4+, respectively. Analysis of the Pt 4f spectra demonstrates that the modification of the Pt/TiO_2 sample with potassium reduces the proportion of Pt^{4+}. At the same time, modification of the catalyst with potassium hydroxide stabilizes platinum in a more reduced state (Pt^0), while modification with potassium chloride stabilize the Pt^{2+} species.

Thus, modification of the samples with potassium chloride is promising for increasing the selectivity of ammonia oxidation towards molecular nitrogen at low temperature range.

This work was supported by the Russian Science Foundation, Grant №23-23-00322.

References:

1. Colombo M., Appl. Catal. B Environ., 2013, 142–143, 337–343.
2. Lan T., Catal. Sci. Tech., 2020, 10, 5792–5810.
3. Torp T.K., Emiss. Control. Sci. Tech., 2021, 7, 7–25.

Transformations of Pd/NHC based catalytic systems under reaction conditions: theoretical and experimental approaches

E. Patil, J. Burykina, A. Kostyukovich, V. Ananikov

Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, Russia

sushchenko@ioc.ac.ru

Palladium complexes with N-heterocyclic carbene ligands (Pd/NHC) are commonly used in organic synthesis. These compounds are not well-defined catalysts and undergo complex transformations in many organic reactions. Pd/NHC complexes form intermediates under reaction conditions that are prone to side processes of reductive elimination with the cleavage of the Pd-C(NHC) bond. As a result of side reactions, "ligand-free" palladium complexes and the H-NHC, R-NHC and O-NHC coupling products are formed. In this work, these processes were studied using a complex of computational (DFT) and physico-chemical (NMR, ESI-MS, TEM) methods.

The key challenge of the study was to determine the contributions of various processes to the transformation of Pd/NHC complexes. However, quantitative estimation of the content of Pd/NHC decomposition products is complicated by the high complexity of reaction systems and low catalyst concentration. This problem was solved using the highly sensitive ESI-MS method, for which selectively deuterated H-NHC, Ph-NHC and O-NHC coupling products were synthesized and used as internal standards. Internal standards were added to the system under study in certain quantities, which made it possible to correlate the peak intensity of each of these compounds with their concentration. This approach made it possible to quantitatively characterize the transformation of the Pd/NHC complex according to three mechanisms of H-NHC, Ph-NHC and O-NHC coupling directly in the Mizoroki-Heck, Sonogashira and transfer hydrogenation catalytic reactions. It was found that in the latter reaction the Pd/NHC complex is predominantly decomposed by the O-NHC coupling pathway, while in the Mizoroki-Heck and Sonogashira reactions the main contribution is made by the H-NHC and Ph-NHC coupling processes, depending on the nature of the ligand. For the Mizoroki-Heck reaction, ESI-MS online monitoring was carried out and kinetic curves of the formation of the corresponding products were obtained. Molecular modeling showed the nonlinear nature of the transformations being studied: at the beginning, the formation of the H-NHC product has the highest rate, which is then slowly consumed into the Ph-NHC product through the reversible addition of H-NHC to the palladium center.

Quantum chemical calculations have shown that the activation energy of the Ph-NHC coupling process in (NHC)Pd(Ph)(I)DMF complexes for different NHC ligands falls within the range of 17.9–25.1 kcal/mol. This process is thermodynamically more favorable for unsaturated NHCs with bulky substituents.

This work was supported by the Russian Science Foundation No 22-73-10109.

References

1. Chernyshev V., Denisova E., Eremin D., Ananikov V., Chem. Sci., 2020, 11, 6957–6977.
2. Kostyukovich A., Tsedilin A., Sushchenko E., Eremin D., Kashin A., Topchiy M., Asachenko A., Nechaev M., Ananikov V., Inorg. Chem. Front., 2019, 6, 482–492.
3. Patil E., Burykina J., Eremin D., Boiko D., Shepelenko K., Ilyushenkova V., Chernyshov V., Ananikov V., Inorg. Chem., 2024, 63, 2967–2976.

SECTION 4

INDUSTRIAL IMPLEMENTATION OF CATALYTIC PROCESSES

Producing cyclopentane from dicyclopentadiene

M.P. Filina[1,2]

[1]*Tomsk State University, Tomsk, Russia*
[2]*Engineering Chemical Technology Centre, Tomsk, Russia*

filina@ect-center.com

Cyclopentane (CPAN), used as a blowing agent for the manufacturing of rigid polyurethane foams with better thermal insulation properties and featuring the least harmful impact on the environment, has now practically replaced freons previously used for these purposes.

In the world practice, the CPAN production comprises its isolation from petroleum and pyrolysis C_5 fractions, while the economic efficiency of the process directly depends on the local amounts of C_5 fraction production. In Russia, such an approach to the CPAN production is becoming economically unfeasible, but the demand in the product can be compensated for by an alternative method of its production, i.e., synthesis from dicyclopentadiene (DCPD). In addition to CPAN, this approach also allows producing a rather valuable cyclopentene (CPEN) used as a monomer for frost-resistant rubbers.

The synthesis of CPAN and CPEN from DCPD proceeds through several stages: thermal cracking of DCPD to obtain cyclopentadiene monomer (CPD) followed by its hydrogenation to CPEN or CPAN on a heterogeneous catalyst with the isolation of the target product by rectification [1].

The work is devoted to the development of the industrially applicable technology to obtain CPEN and CPAN from the DCPD in a combined reaction-distillation process. The results of experimental studies of the process to obtain CPAN from DCPD and the features of CPD hydrogenation in a reaction-rectification unit at the pilot plant scale with the DCPD capacity of 360 g/h are presented in the publication [2].

The CPD hydrogenation process was carried out both on the Al-Pd catalyst (Polymax 200) as well as the kieselguhr-supported Ni catalyst, which is widely used in industry.

During the studies, a significant temperature gradient was found to form along the top of the hydrogenation catalyst layer. The temperature of the upper catalyst layer reached 170 °C. This circumstance imposed a number of additional requirements on the equipment and catalyst loading profile during the industrial implementation of the process in the case of the CPEN production as a target product.

According to the results of experimental studies, a lower catalytic activity of the kieselguhr-supported Ni catalyst was established in comparison with the Al-Pd catalyst in the hydrogenation of the CPD monomer. The reaction mass obtained under equal conditions in the case of the Ni-containing catalyst was enriched with unreacted feed by an average of 7% higher than in the case of the Al-Pd sample. In addition, a significant shift in the equilibrium towards the CPAN formation under the process conditions should be noted due to the CPEN conversion on the Al-Pd catalyst (75.8%) as compared to the nickel-based catalyst (56.6%).

The results of the study of the CPD hydrogenation process allow us to draw a conclusion about the possibility of its implementation in industry in the reaction-distillation process using the catalytic systems based on precious metals or those with deposited Ni, while in order to ensure “soft” hydrogenation conditions to obtain CPEN, it is necessary to work out in detail both the hardware design of the reaction zone of the apparatus and to ensure the correct calculation of the catalyst loading profile to optimize the temperature gradient across the layer.

This work was supported by the IVF of the Republic of Tatarstan.

References

1. Hönicke D, Födisch R, Claus P, Olson M., Cyclopentadiene and cyclopentene. In: Ullmann's encyclopedia of industrial chemistry, Weinheim: Wiley-VCH, 2002.
2. Bayguzin F.A., Burmistrov D.A., Irdinkin S.A., Filina M.P., Catalysis in industry, 2018, 1, 6–12.

Surfactant-assisted sulfuric acid catalyzed motor fuel alkylation approach

A.V. Nikityonok, D.P. Ivanov, D.E. Babushkin, A.O. Kuzmin

Boreskov Institute of Catalysis, Novosibirsk, Russia

nikitenoka@catalysis.ru

Liquid acid catalyzed alkylation reaction of isobutane by olefins is one of the important industrial processes. It produces the highly valuable component of gasoline – alkylate, which is a mixture of highly branched alkanes, preferably trimethylpentanes. This alkylate is characterized by: high-octane numbers, the absence of sulfur and zero aromatics content, and clean burn leads to practically zero vehicle tailpipe emission. Additionally, and critically, alkylate has very low fuel volatility.

Today, majority of alkylate in refineries is produced using two main technologies: one based on water-free hydrofluoric acid (HF) and the other on 96-98% sulfuric acid (H_2SO_4). Currently there are over 200 sulfuric acid alkylation units (SAAU) and less than 100 hydrogen fluoride units globally. Comparatively, in the Russian Federation there are only about 10 alkylation units with an industrial capacity of merely 0.5 million tons per year, contrasting with global production of over 70 million tons annually [1].

The trend in recent years is to remove HF alkylation units due to the high HF hazardous. The main issue of sulfuric acid catalyzed alkylation is the low solubility of isobutane and high solubility of butene-1 in H_2SO_4. This leads to numerous side-reaction with acid-soluble oils (ASO) formation. As a result, alkylate quality decreases and high acid consumption (up to 50-90 kg of pure H_2SO_4 per 1 ton of product) could be observed. Finally, nearly 30% of all operational cost of sulfuric acid alkylation units is the cost of expenses tied with H_2SO_4.

This work presents the research results of principally new surfactant systems aimed to improve the sulfuric acid alkylation reaction.

For the first time it was found the new surfactant and co-surfactant systems, stable in concentrated H_2SO_4 media, capable to form the thermodynamically stable Winsor type III microemulsion alkane-acid systems. The distinct feature of Winsor III microemulsions is the near-zero surface tension which leads to fast interphase surface renovation and maximal solubilization effect of immiscible components [2]. The surfactant/co-surfactant mixtures found are: stearic acid + perfluorated sulfuric acid and dimethyldioctadecyl ammonium chloride. Even small amount of this surfactant's mixture (about 0.03 wt.%) allows to drastically enhance the key parameters of alkylation process.

Experimental results are summarized below:

- Research Octane Number (RON) of alkylate obtained with modified system is higher than 100 (93-95 RON for industrial processes) [3, 4];
- 1-butene selectivity is increased by 1.5 compared with the pure H_2SO_4 is used as catalyst;
- Alkylate yield is increased by 1.4 with enhancing auto-alkylation route of the reaction;
- ASO accumulates more than 10 times slower – same amount of H_2SO_4 could be used much longer.

This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the governmental assignment for Boreskov Institute of Catalysis (project FWUR-2024-0038).

References

1. Akhmadova K.K. et. al., Theoretical Foundations of Chemical Engineering, 2019, 4 (53), 643–655.
2. Salager J.-L. and et al., J. Surfactants Deterg., 2005, 8 (1), 3–21.
3. Kuzmin A.O., Nikityonok A.V., RU Patent 2815695 C1, 2024.
4. Bkhattachariiya A., Briker D.K., Rajli M.G, Kuzmin A.O., RU Patent 2782562 C2, 2022.

Table of contents

PLENARY LECTURES

KEYNOTE LECTURES

SECTION 1
CATALYST PREPARATION

SECTION 2
PROMISING CATALYTIC PROCESSES

SECTION 3
PHYSICAL-CHEMICAL FUNDAMENTALS OF CATALYSIS

SECTION 4
INDUSTRIAL IMPLEMENTAITION OF CATALYTIC PROCESSES

Scientific edition

CATALYSIS: FROM SCIENCE TO INDUSTRY

Proceedings of
VIII International scientific school-conference for young scientists

September 30 - October 3, 2024

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

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 11.09.2024. Format 60×84$_{1/8}$. Offset paper
№1. Offset print. Printed sheets 15,2.
Order №6012. Number of copies 500 issues.

ISBN 978-5-907722-99-6