

ISSN 2518-1491 (Online),
ISSN 2224-5286 (Print)

ҚАЗАҚСТАН РЕСПУБЛИКАСЫ
ҰЛТТЫҚ ҒЫЛЫМ АКАДЕМИЯСЫНЫҢ

Д.В. Сокольский атындағы «Жанармай,
катализ және электрохимия институты» АҚ

Х А Б А Р Л А Р Ы

ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
АО «Институт топлива, катализа и
электрохимии им. Д.В. Сокольского»

NEWS

OF THE ACADEMY OF SCIENCES
OF THE REPUBLIC OF KAZAKHSTAN
JSC «D.V. Sokolsky institute of fuel, catalysis
and electrochemistry»

SERIES
CHEMISTRY AND TECHNOLOGY

4 (442)

JULY – AUGUST 2020

PUBLISHED SINCE JANUARY 1947

PUBLISHED 6 TIMES A YEAR

ALMATY, NAS RK

NAS RK is pleased to announce that News of NAS RK. Series of chemistry and technologies scientific journal has been accepted for indexing in the Emerging Sources Citation Index, a new edition of Web of Science. Content in this index is under consideration by Clarivate Analytics to be accepted in the Science Citation Index Expanded, the Social Sciences Citation Index, and the Arts & Humanities Citation Index. The quality and depth of content Web of Science offers to researchers, authors, publishers, and institutions sets it apart from other research databases. The inclusion of News of NAS RK. Series of chemistry and technologies in the Emerging Sources Citation Index demonstrates our dedication to providing the most relevant and influential content of chemical sciences to our community.

Қазақстан Республикасы Ұлттық ғылым академиясы "ҚР ҰҒА Хабарлары. Химия және технология сериясы" ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Web of Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Химия және технология сериясы Emerging Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді химиялық ғылымдар бойынша контентке адалдығымызды білдіреді.

НАН РК сообщает, что научный журнал «Известия НАН РК. Серия химии и технологий» был принят для индексирования в Emerging Sources Citation Index, обновленной версии Web of Science. Содержание в этом индексировании находится в стадии рассмотрения компанией Clarivate Analytics для дальнейшего принятия журнала в the Science Citation Index Expanded, the Social Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество и глубину контента для исследователей, авторов, издателей и учреждений. Включение Известия НАН РК в Emerging Sources Citation Index демонстрирует нашу приверженность к наиболее актуальному и влиятельному контенту по химическим наукам для нашего сообщества.

Б а с р е д а к т о р ы
х.ғ.д., проф., ҚР ҰҒА академигі
М.Ж. Жұрынов

Р е д а к ц и я а л қ а с ы:

Ағабеков В.Е. проф., академик (Белорус)
Баешов А.Б. проф., академик (Қазақстан)
Бүркітбаев М.М. проф., академик (Қазақстан)
Волков С.В. проф., академик (Украина)
Воротынцев М.А. проф., академик (Ресей)
Газалиев А.М. проф., академик (Қазақстан)
Джусипбеков У.Ж. проф., корр.-мүшесі (Қазақстан)
Жармағамбетова А.К. проф. (Қазақстан), бас ред. орынбасары
Жоробекова Ш.Ж. проф., академик (Қырғыстан)
Иткулова Ш.С. проф. (Қазақстан)
Манташян А.А. проф., академик (Армения)
Пралиев К.Д. проф., академик (Қазақстан)
Рахимов К.Д. проф., академик (Қазақстан)
Рудик В. проф., академик (Молдова)
Стрельцов Е. проф. (Белорус)
Тельтаев Б.Б. проф., академик (Қазақстан)
Тодераш И. проф., академик (Молдова)
Тулеуов Б.И. проф., академик (Қазақстан)
Фазылов С.Д. проф., академик (Қазақстан)
Фарзалиев В. проф., академик (Әзірбайжан)
Халиков Д.Х. проф., академик (Тәжікстан)
Шайхутдинов Е.М. проф., академик (Қазақстан)

«ҚР ҰҒА Хабарлары. Химия және технология сериясы».

ISSN 2518-1491 (Online),

ISSN 2224-5286 (Print)

Меншіктенуші: «Қазақстан Республикасының Ұлттық ғылым академиясы» Республикалық қоғамдық бірлестігі (Алматы қ.).

Қазақстан Республикасының Ақпарат және қоғамдық даму министрлігінің Ақпарат комитетінде 29.07.2020 ж. берілген № **KZ66VPY00025419** мерзімдік басылым тіркеуіне қойылу туралы куәлік.

Мерзімділігі: жылына 6 рет.

Тиражы: 300 дана.

Редакцияның мекенжайы: 050010, Алматы қ., Шевченко көш., 28; 219, 220 бөл.; тел.: 272-13-19; 272-13-18,
<http://chemistry-technology.kz/index.php/en/arhiv>

© Қазақстан Республикасының Ұлттық ғылым академиясы, 2020

Редакцияның мекенжайы: 050100, Алматы қ., Қонаев к-сі, 142, «Д. В. Сокольский атындағы отын, катализ және электрохимия институты» АҚ, каб. 310, тел. 291-62-80, факс 291-57-22, e-mail:orgcat@nursat.kz

Типографияның мекенжайы: «NurNaz GRACE», Алматы қ., Рысқұлов көш., 103.

Главный редактор
д.х.н., проф., академик НАН РК
М.Ж. Журинов

Редакционная коллегия:

Агабеков В.Е. проф., академик (Беларусь)
Баешов А.Б. проф., академик (Казахстан)
Буркитбаев М.М. проф., академик (Казахстан)
Волков С.В. проф., академик (Украина)
Воротынцев М.А. проф., академик (Россия)
Газалиев А.М. проф., академик (Казахстан)
Джусипбеков У.Ж. проф., чл.-корр. (Казахстан)
Жармагамбетова А.К. проф. (Казахстан), зам. гл. ред.
Жоробекова Ш.Ж. проф., академик (Кыргызстан)
Иткулова Ш.С. проф. (Казахстан)
Манташян А.А. проф., академик (Армения)
Пралиев К.Д. проф., академик (Казахстан)
Рахимов К.Д. проф., академик (Казахстан)
Рудик В. проф., академик (Молдова)
Стрельцов Е. проф. (Беларусь)
Тельтаев Б.Б. проф., академик (Казахстан)
Тодераш И. проф., академик (Молдова)
Тулеев Б.И. проф., академик (Казахстан)
Фазылов С.Д. проф., академик (Казахстан)
Фарзалиев В. проф., академик (Азербайджан)
Халиков Д.Х. проф., академик (Таджикистан)
Шайхутдинов Е.М. проф., академик (Казахстан)

«Известия НАН РК. Серия химии и технологий».

ISSN 2518-1491 (Online),

ISSN 2224-5286 (Print)

Собственник: Республиканское общественное объединение «Национальная академия наук Республики Казахстан» (г. Алматы).

Свидетельство о постановке на учет периодического печатного издания в Комитете информации Министерства информации и общественного развития Республики Казахстан № KZ66VPY00025419, выданное 29.07.2020 г.

Периодичность: 6 раз в год.

Тираж: 300 экземпляров.

Адрес редакции: 050010, г. Алматы, ул. Шевченко, 28; ком. 219, 220; тел. 272-13-19; 272-13-18,
<http://chemistry-technology.kz/index.php/en/arhiv>

© Национальная академия наук Республики Казахстан, 2020

Адрес редакции: 050100, г. Алматы, ул. Кунаева, 142, АО «Институт топлива, катализа и электрохимии им. Д.В. Сокольского», каб. 310, тел. 291-62-80, факс 291-57-22, e-mail:orgcat@nursat.kz

Адрес типографии: «NurNaz GRACE», г. Алматы, ул. Рыскулова, 103.

Editor in chief

doctor of chemistry, professor, academician of NAS RK

M.Zh. Zhurinov

Editorial board:

Agabekov V.Ye. prof., academician (Belarus)
Bayeshov A.B. prof., academician (Kazakhstan)
Burkitbayev M.M. prof., academician (Kazakhstan)
Volkov S.V. prof., academician (Ukraine)
Vorotyntsev M.A. prof., academician (Russia)
Gazaliyev A.M. prof., academician (Kazakhstan)
Dzhusipbekov U.Zh. prof., corr. member (Kazakhstan)
Zharmagambetova A.K. prof. (Kazakhstan), deputy editor in chief
Zhorobekova Sh.Zh. prof., academician (Kyrgyzstan)
Itkulova Sh.S. prof. (Kazakhstan)
Mantashyan A.A. prof., academician (Armenia)
Praliyev K.D. prof., academician (Kazakhstan)
Rakhimov K.D. prof., academician (Kazakhstan)
Rudik V. prof., academician (Moldova)
Streltsov Ye. prof. (Belarus)
Teltaev B.B. prof., akademik (Kazakhstan)
Toderash I. prof., academician (Moldova)
Tuleuov B.I. prof., akademik (Kazakhstan)
Fazylov S.D. prof., akademik (Kazakhstan)
Farzaliyev V. prof., academician (Azerbaijan)
Khalikov D.Kh. prof., academician (Tadjikistan)
Shaihutdinov E.M. prof., akademik (Kazakhstan)

News of the National Academy of Sciences of the Republic of Kazakhstan. Series of chemistry and technology.

ISSN 2518-1491 (Online),

ISSN 2224-5286 (Print)

Owner: RPA "National Academy of Sciences of the Republic of Kazakhstan" (Almaty).

The certificate of registration of a periodical printed publication in the Committee of information of the Ministry of Information and Social Development of the Republic of Kazakhstan **No. KZ66VPY00025419**, issued 29.07.2020.

Periodicity: 6 times a year.

Circulation: 300 copies.

Editorial address: 28, Shevchenko str., of. 219, 220, Almaty, 050010, tel. 272-13-19; 272-13-18,

<http://chemistry-technology.kz/index.php/en/arhiv>

© National Academy of Sciences of the Republic of Kazakhstan, 2020

Editorial address: JSC «D.V. Sokolsky institute of fuel, catalysis and electrochemistry», 142, Kunayev str., of. 310, Almaty, 050100, tel. 291-62-80, fax 291-57-22, e-mail: orgcat@nursat.kz

Address of printing house: «NurNaz GRACE», 103, Ryskulov str, Almaty.

L. R. Sassykova¹, N. E. Maximov¹, A.Y.Yerzhanov¹, M. S. Ilmuratova¹, A.T.Raiyssov¹,
Y. A. Aubakirov¹, R.N. Azhigulova¹, A.A. Batyrbayeva¹, S. Sendilvelan²

¹Faculty of Chemistry and Chemical Technology, Al-Farabi Kazakh National University, Almaty, Kazakhstan;

²Department of Mechanical Engineering, Dr. M.G.R Educational and Research Institute, University, Chennai, India.

E-mail: larissa.rav@mail.ru, narimaksimov@gmail.com, arman689396@gmail.com, ilmuratova97@mail.ru,
araiyssov2014@gmail.com, miral.64@mail.ru, razhigulova@gmail.com, batyrbaeva_aigul@mail.ru,
sendilvelan63@gmail.com.

EFFECTIVE CATALYSTS FOR THE SELECTIVE RESTORATION OF AROMATIC MONO- AND DINITRO COMPOUNDS

Abstract. This article discusses the issues of catalytic reduction of aromatic nitro compounds to obtain valuable intermediate and final products-aromatic amines. The most important method for producing amines from nitro compounds is catalytic reduction with hydrogen on catalysts. The article describes in detail the choice of catalysts for hydrogenation of nitro compounds at atmospheric and high hydrogen pressure. Studies of hydrogenation reactions of aromatic nitro compounds on nickel, copper and iron catalysts are discussed. Hydrogenation of aromatic nitro compounds on catalysts based on palladium, platinum, and rhodium deposited on various carriers, including nanodiamonds, is considered. Catalysts based on supported palladium catalysts with copper additives showed high selectivity in the hydrogenation of nitro groups in nitro compounds with functional groups; and with the addition of platinum and rhodium, during the reduction of both nitro groups and the aromatic ring in nitrobenzene. In the works on the use of nanodiamonds, it was found that catalysts based on platinum and palladium nanoparticles of 4-5 nm in size, fixed on nanodiamonds, were highly active in liquid-phase hydrogenation reactions of nitro compounds under mild conditions. The data described by the authors on theoretical issues and practical problems of catalytic hydrogenation of aromatic nitro compounds are very relevant. The article is based on the analysis of domestic and foreign literature and may be useful to specialists in the field of catalysis.

Keywords: aromatic nitro compounds, catalytic reduction, aromatic amines, selective catalysis, liquid-phase hydrogenation.

Introduction. Nitro compounds are derivatives of hydrocarbons of the general formula R-NO₂ having in their composition a nitro group directly linked to an aliphatic or aromatic radical. Depending on the nature of the hydrocarbon radical “R”, nitro compounds are divided into aliphatic and aromatic. The simplest representative of nitro compounds of the aliphatic series is nitromethane, chemical compound with the formula CH₃-NO₂. Aliphatic nitro compounds are divided into primary, secondary and tertiary. Compounds containing several nitro groups, when heated or detonation decompose with an explosion, therefore many of them found application as explosives. Nitro groups (especially in symmetric trinitro compounds) greatly increase the ability of a carbon atom located in the ortho position to nitro groups to oxidize. The most important property of the nitro group is its ability to be reduced to an amino group. Amines find wide application in the production of various dyes, drugs, corrosion inhibitors, stabilizers, polyurethanes, antiknock additives for gasolines and motor fuels and others [1-4]. Amines are organic compounds that are derivatives of ammonia, in the molecule of which one, two or three hydrogen atoms are replaced by hydrocarbon radicals. A typical representative of a number of aromatic amines is aniline.

In the last 30-40 years, the processes of catalytic reduction of aromatic nitro compounds by hydrogen to amines have practically superseded all other methods for the production of aromatic amines in large-tonnage plants.

Catalysts for nitro compounds hydrogenation. One of the topical areas is the development and investigation of highly efficient and selective catalysts for the hydrogenation of aromatic nitro compounds to the corresponding amines, since amines find wide application in the production of various dyes, drugs, corrosion inhibitors, stabilizers, polyurethanes, antiknock additives for gasolines and motor fuels and others. The reduction of nitro compounds can be carried out in the presence of both homogeneous and heterogeneous catalysts. Solid phase heterogeneous catalysts are widely used in industry. This is due to the difficulty in isolating and regenerating a homogeneous catalyst. Heterogeneous hydrogenation catalysts for aromatic nitro compounds [5] can be divided into the following groups: 1) catalysts containing nickel, copper and noble metals, including blacks; 2) heterogeneous catalysts on a fiberglass woven matrix; 3) heterogeneous catalysts on a metal-polymeric matrix. An important role as a part of the catalyst is played by the carrier. Carriers for catalysts use various carbon carriers: activated carbon, carbon fiber, nanodiamond, fullerene black, as well as various oxides such as Al_2O_3 , SiO_2 , CaCO_3 ; polymeric, fiberglass and other matrices. Recently, carbon nanomaterials have been used as a catalyst carrier: fullerenes and fullerene black, carbon nanotubes and nanofibres, nanodiamonds and graphene materials. Particular interest is given to nanodiamonds (ND) and graphene-like materials. ND have unique properties: high strength, high specific surface with different functional groups located on it, which can be easily modified.

The hydrogenation of nitrobenzene is one of the model reactions for studying the activity of samples of potential catalysts. Most studies of the reduction of nitro compounds, as shown by the analysis of patents and literature data, are carried out using nickel catalysts [6]. The most common catalyst for the reduction of various objects, including nitro compounds, is currently Raney nickel. Skeletal nickel catalyst was developed by M. Raney in 1924-1925. Raney Nickel, obtained from alloys of Ni with Mg or Zn, has a much lower catalytic activity in most reactions. The skeletal nickel catalyst has a structure of metallic nickel with crystal sizes of 4-8 nm. It varies little with prolonged storage under a 1% solution of NaOH. The magnitude of nickel crystals depends on the leaching temperature, increasing with the growth of the latter. This is very important, since for each hydrogenated compound there is an optimal crystal size, which, for example, for the reduction of NB is 5.9 nm, for phenol hydrogenation - 3.0 nm. The reactivity of nickel is heavily influenced by leaching conditions, in particular temperature, which determine both the activity of the surface and the strength of hydrogen retention.

The supported catalysts are widely used in processes with both a mobile and a stationary catalyst bed. A very important role in their performance (running time, longevity, activity, mechanical strength, etc.) is played by the nature of the carrier. The most common among the latter are silicon and aluminum oxides. As in the production of Raney nickel, the production of supported nickel catalysts is determined by the conditions of metal deposition, the reduction temperature of the catalyst, and the degree of saturation with hydrogen. In the work [7], bimetallic Fe-Cu/ SiO_2 systems were proposed for the process of liquid-phase hydrogenation of p-dinitrobenzene to p-phenylenediamine.

Palladium is of particular interest for theoretical chemistry due to its position in the periodic table: it is the only element with the electronic configuration $d^{10}s^0p^0$, which can vary depending on the type of chemical binding and determines the specific behavior of this metal. It was shown that catalysts based on deposited palladium catalysts with copper additives have shown high selectivity in hydrogenation of nitrogroups in nitro compounds with functional groups. Thus a catalyst with composition Pd-Cu(9:1)/sibunit, Pd-Cu(8:2)/sibunit was active in a case of selective obtaining 4,4'-diaminostilbene-2,2'-disulfonic acid (DAS) by hydrogenation of 4,4'-dinitrostilbene-2,2'-disulfonic acid (trans-DNS) in water. DAS can be used to produce phosphorescent whiteners for fibers and paper. Catalysts based on supported palladium catalysts with the addition of platinum and rhodium showed high selectivity during hydrogenation during the reduction of both nitro groups and the aromatic ring in nitrobenzene using isopropanol and ethanol as solvents [2, 3, 8]. The role of palladium in catalytic reactions is largely determined by the different structure of active sites on its surface. As is known, the first stage of catalytic hydrogenation is the adsorption of hydrogen and substrates on the surface of the catalyst [9-12]. Regarding the forms and methods of activating hydrogen on the active centers of hydrogenation catalysts in the literature there are different viewpoints. The relative inertness of hydrogen is due to the high dissociation energy of its molecule ($432.9 \text{ kJ} \times \text{mol}^{-1}$). The bond between the H_2 atoms can be weakened by donor-acceptor coordination with a metal in which hydrogen can act as both a donor and an electron acceptor to form charged particles of $\text{H}_2^{\delta+}$ and $\text{H}_2^{\delta-}$, whose dissociation energies (259.6 and $77.9 \text{ kJ} \times \text{mol}^{-1}$,

respectively) is much lower than the dissociation energy of the H_2 molecule. On the metal surface there are at least four hydrogen forms having different reactivity in liquid-phase hydrogenation processes: weakly bound molecular $H_2^{\delta+}$, as well as tightly atomic hydrogen: ionized $H_2^{\delta+}$, $H_2^{\delta-}$ and unionized H between which is set the adsorption equilibrium [13].

The values of adsorption, charges, binding energies and the ratio of different forms of hydrogen depend both on the nature and dispersity of the catalyst, and on the nature of the solvent. In addition to these forms, dissolved hydrogen is present in the volume of the metal, which penetrates into the crystal lattice of palladium through sites adsorbing weakly bound molecular forms (adsorption heat of $7 \text{ kJ} \times \text{g} \cdot \text{atom}^{-1}$). Calculation of the thermal effects of all stages of hydrogen sorption based on the results of the microbalance experiment showed that the dissolution of hydrogen in palladium is energetically more favorable (activation energy $15 \text{ kJ} \times \text{g} \cdot \text{atom}^{-1}$) than its migration along the surface to centers with a higher heat of adsorption (activation energy $55 \text{ kJ} \times \text{g} \cdot \text{atom}^{-1}$). During dissolution, a multicenter bonding of hydrogen to palladium can take place, in particular, in the case of the Pd/Al₂O₃ catalyst, up to 5 hydrogen atoms can be adsorbed on one Pd atom.

The behavior of palladium in catalytic processes is associated with different geometric structures of the active centers of its surface. According to D.V. Sokolsky [5, 6, 13], hydrogen on the surface of metals exists in a "predissociative form", in which the H-metal bond is stronger than the H-H bond. The results of quantum chemical calculations, which were carried out later, are consistent with this statement. The choice of the optimum catalysis in the case of catalytic hydrogenation can be solved with its preliminary electrochemical characteristics. The measurement of the potential of the catalyst immediately gives an answer to the question of the type of reaction. Thanks to the application of electrochemical methods, developed by the catalytic school of D.V. Sokolsky, it became possible to determine the concentrations of reactants on the surface of catalysts during the reaction, of particular importance in the practice of catalytic hydrogenation has been the application of these methods to powder catalysts. The method of liquid hydrogenation is now one of the most developed methods in the theoretical and practical relation. In contrast, the gas-phase reduction of aromatic nitro compounds requires the use of high temperatures to ensure the evaporation of the nitro compounds. Solvent can influence both for the rate, and the reaction mechanism. Rate of diffusion depends on viscosity of solvent. Rates of the chemical reactions can sufficiently change depending on the solvent nature. A high degree of chemo-, regio-, stereoselectivity of catalysts in the reactions of hydrogenation is very important. Catalysts based on metals of the platinum group: metal black and supported catalysts have found wide application for the production of amines. Catalytic systems based on platinum group metals deposited on various sorbents reveal higher activity and stability than nickel catalysts. In the earliest works (50-70 years of XX century) the catalyst, regardless of its composition, was used in amounts equal to or exceeding several times the amount of hydrogenated nitro compound. It should be noted that the black metal due to their properties, did not find practical application in the production of amines. At the same time, platinum metals deposited on various carriers, even at low contents, show high activity and selectivity of action during the reduction of aromatic nitro compounds.

Despite the high cost, the catalysts based on platinum group metals are widely used in the hydrogenation of organic compounds, in particular, for the production of aromatic amines from the corresponding nitro compounds. A special role in this is played by the catalysts of the platinum group deposited on various carriers [8, 14]. The reduction of 3,4-dichloronitrobenzene in the presence of iridium and platinum catalysts was studied and it was established that the limiting stage of the process is the step of converting the corresponding arylhydroxylamine into an amino compound. The orders of the reaction along the substrate and hydrogen are calculated, and the optimum process conditions are determined.

Platinum and palladium catalysts deposited on coal showed high activity and stability in the reduction of nitrobenzene, nitroanilines, p- and o-nitrophenols and other nitro compounds with various substituents. Palladium-containing catalysts differ significantly in properties from catalytic systems based on other metals of the platinum group, as well as Ni or Cu. Pd-based catalysts are one of the most effective catalytic systems for the hydrogenation of double (also conjugated) and triple bonds. In cases where it is necessary to hydrogenate only nitro groups in aromatic nitro compounds, without affecting the double bonds of the aromatic ring, it is necessary to use Pd-systems.

To improve the processes of organic and inorganic synthesis, catalysts based on rare-earth elements are increasingly being used. Rare-earth elements are used as an active phase, promoting additives, and

their oxides are used as a carrier. In some works [14, 15] it is pointed out that one of the directions of use of rare and platinum metals is associated with the development of catalysts for various purposes. For example, deep oil processing involves a variety of catalytic processes using Re, Pt, Pd-containing catalysts. Hydrogenation in the liquid phase of nitrobenzene, o-nitroanisole, p-nitrotoluene, p-nitrophenol, chloronitrobenzene, 1,3,5-trinitrobenzene in Pd and Pt catalysts with rare earth metal oxide additives was studied. The highest process speed was detected using catalysts with additives Gd_2O_3 , Tb_2O_3 , Dy_2O_3 . It was found that the activity of 1% Pt/ Gd_2O_3 catalyst exceeds the activity of the catalyst 1% Pt/ Al_2O_3 by 3.5 times, and the activity of 1% Pt/ Sm_2O_3 catalyst is higher than the activity of 1% Pt/ Al_2O_3 by 3.2 times. Authors found that the activity of platinum-based catalysts containing Eu_2O_3 and Sm_2O_3 in the hydrogenation of nitrobenzene by a potentiometric method was studied. Analysis of the products of the hydrogenation reaction of nitrobenzene on 1% Pt catalysts containing oxides of Eu_2O_3 , Sm_2O_3 and Al_2O_3 as carriers by gas-liquid chromatography showed the presence of only one product, aniline, which indicates a high selectivity of hydrogenation. Metal-containing graphene materials proved to be catalytically active, stable and selective in hydrogenation reactions. It is of interest to obtain Pd-containing catalysts based on nanodiamonds and amine-functionalized graphite oxide and to study their catalytic properties in model hydrogenation reactions of compounds with different chemical bonds (nitro group, $>C=C<$ and $>C=N<$ bonds) and also to compare the obtained characteristics with the catalyst on activated carbon prepared by a similar procedure. The Pt/ TiO_2 /RGO catalyst in the hydrogenation of nitrobenzene without a solvent showed high selectivity and activity ($TOF = 59,000\ h^{-1}$) as compared to Pt/ TiO_2 and Pt/RGO in 2.6 and 1.7 times, respectively. In addition, the catalyst can be reused for six times without loss of activity. The authors conclude that the catalyst structure is stable. In comparison, Pt/ TiO_2 catalytic activity decreases by about 40% already in the second cycle, but Pt/RGO retains good catalytic activity after three cycles of use in hydrogenation. A study of the catalytic properties of Pt/NB and Pd/ND (ND-nanodiamonds) in the hydrogenation of NB showed that the catalysts have high activity and stability, as well as selectivity: aniline is the only reaction product (no by-products formed, which was confirmed analysis of reaction mixtures by gas chromatography) [16-19] (fig.1). Physicochemical analyzes of carriers (ND, activated carbon of M200 grade) and catalysts based on them (1 wt% Pd/ND, 1 wt% Pd/C) by SEM, energy dispersive X-ray spectroscopy (EDX) were carried out, as well as the XPS. The structure of the used carriers was used by the SEM method: M20 activated carbon (fig.2a) and ND (fig.2b). In fig. 2b it is visible that the structure of ND represents fractal system with various size of separate grains whereas the structure of activated carbon (fig.2a) consists of separate graphite flakes of various forms and the sizes.

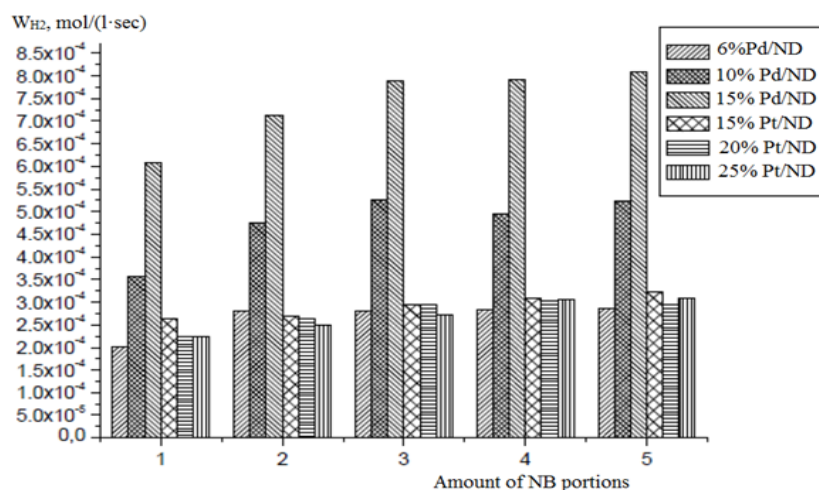


Figure 1 - Velocity of hydrogenation reaction of nitrobenzene

Comparing the results of the analysis of catalysts, it can be stated that palladium fixed to ND does not wash off during the reaction from the carrier, whereas, in the case of Pd/C, metal losses amounted to almost 50% of the initial content. This may be the result of the participation of nitrogen-containing groups

of ND (amino or amide) in the process of palladium fixation. Indeed, in the XPS spectra before and after the reaction in the presence of Pd/ND the presence of nitrogen is fixed, while the Pd/C is not. In Pd/C part of the metal (7-9%) is in places inaccessible to the reductant and therefore remains inactive. After the reaction in both catalysts, the main peaks shift both Pd_{3d_{5/2}} and Pd_{3d_{3/2}} towards higher binding energies, apparently due to partial oxidation of the metal centers by formation of surface complexes with charge transfer from palladium to nitrobenzene. In addition, the nature of the carrier affects the binding energy of the palladium electrons. In the case of ND, this value at Pd_{3d_{5/2}} level is 335.0 eV, whereas for coal it is 335.3 eV.

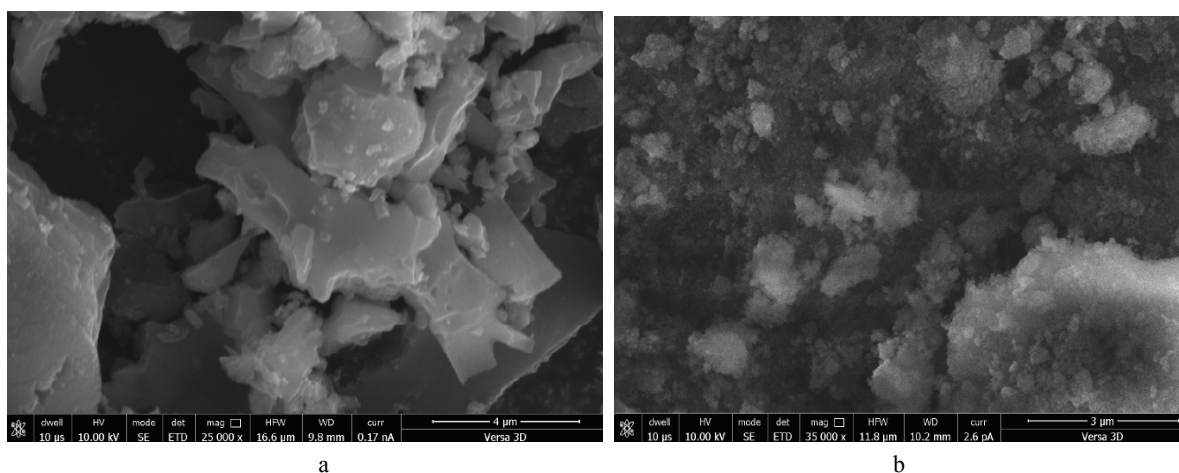


Figure 2 - SEM image of activated carbon M200 (a) and ND (b)

Properties of 1 wt. % Pd/ND and 1 wt. % Pd/C were studied in the hydrogenation reactions of nitrobenzene and its para-substituted analogues (p-nitroaniline, p-nitrophenol, p-nitrobenzoic acid), as well as cyclohexene, hexene-1, allyl alcohol, acrylic, methacrylic, crotonic and cinnamic acids (fig.3). The proposed substrates differ in the nature and location of the groups being reduced, which makes it possible under comparable conditions to trace the influence of the nature of the catalyst on the kinetic parameters of hydrogenation, and also to study the effect of the substituent in nitroarenes on the rate of reduction of the NO₂ group. In the hydrogenation of nitrobenzene and its para-substituted analogs (p-nitroaniline, p-nitrophenol, p-nitrobenzoic acid), 1 wt. % Pd/ND is more active than 1 wt. % Pd/C. Apparently, the NO₂-group is sterically more accessible for contact centers of the catalyst of 1 wt. % Pd/ND and worse for catalyst 1 wt. % Pd/C, which can be explained by the strictly ordered nanoscale structure of ND in comparison with activated carbon, in the structure of which there are pores of various diameters [20], where, apparently, a part of palladium is fixed, thereby becoming inaccessible to the substrate molecules. However, judging by the XPS data, the proportion of palladium that is not reduced does not exceed 7-9%. The hydrogenation of nitrobenzene is most easily carried out for each of the catalysts.

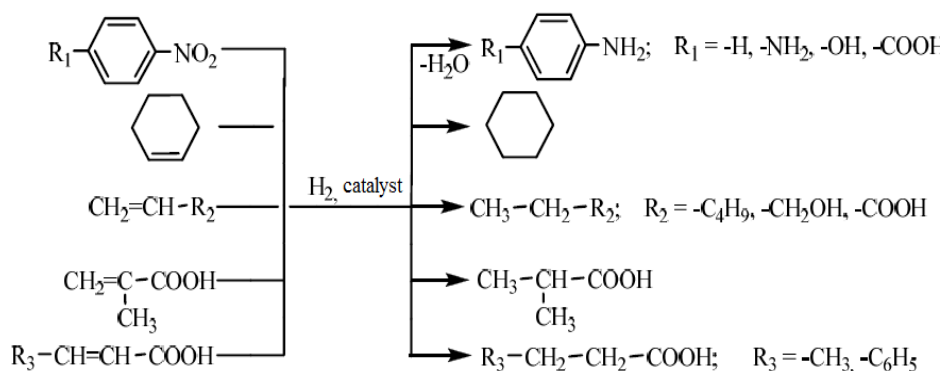


Figure 3 - Scheme of substrate transformation in model hydrogenation reactions

Conclusion. This article provides a brief overview of the studies of the catalytic reduction of aromatic nitro compounds to the corresponding amines. Increasing attention of chemists is attracted by the possibility of using nitro derivatives for the needs of industry and agriculture, both directly and as a relatively cheap chemical material in the synthesis of various products with high applied value. A special place among the chemical transformations of nitro compounds is occupied by the reduction reaction. There is no need to dwell on the enormous industrial significance of this reaction in the aromatic series. Studies of hydrogenation reactions of aromatic nitro compounds on nickel, copper and iron catalysts are described. Hydrogenation of aromatic nitro compounds on catalysts based on palladium, platinum, and rhodium deposited on various carriers, including nanodiamonds, is considered. Data interpretation was carried out using materials published in domestic and foreign sources.

Л.Р. Сасыкова¹, Н.Е. Максимов¹, А.Е. Ержанов¹, М.С. Илмуратова¹, А.Т. Райысов¹,
Е.А. Әубәкіров¹, Р.Н. Ажигулова¹, А.А. Батырбаева¹, С.Сендилвелан²

¹Әл-Фараби атындағы Қазақ ұлттық университеті, Алматы, Қазақстан;

²Department of Mechanical Engineering, DR.M.G.R. Educational
and Research Institute, University, Chennai, Tamilnadu, India

АРОМАТТЫ МОНО ЖӘНЕ ДИНИТРОҚОСЫЛЫСТАРДЫ СЕЛЕКТИВТІ ТОТЫҚСЫЗДАНДЫРУДЫҢ ТИІМДІ КАТАЛИЗАТОРЛАРЫ

Аннотация. Мақалада ароматты нитро қосылыстарды катализдік тотықсыздандыру арқылы маңызды аралық және соңғы өнім – ароматты аминдерді алу қарастырылған. Өртүрлі алуан синтетикалық бояғыш (сурет, бояу өнеркәсібі, табиғи және синтетикалық талшықтарды бояуда), фотохимикат, отын тұрақтандырғыш пен қоспа, жағармай, өсімдікті химиялық қорғау құралы, синтетикалық талшық, сорбент, дәрілік заттарды және т.б. алу өндірісінде жоғары реакциялық қабілетіне сәйкес ароматты моно-, ди- және полиаминдер кеңінен қолданылады. Аминді алудың маңызды жолының бірі – нитроқосылыстарды сутекпен катализатор қатысында тотықсыздандыру. Нитроқосылыстарды катализдік тотықсыздандыруда КСРО, ТМД елдері, Ресей және Қазақстан ғалымдары үлкен үлес қосты. Қазіргі уақытта кейбір елдерде ТМД-ны қоса алғанда, нитроқосылыстарды еріткіш қатысында тотықсыздандыру арқылы амин алу – негізгі әдістердің бірі. Еріткіштерді қолдану нәтижесінде үдеріс бу әдісімен гидрлеуге қарағанда жеңіл жағдайда жүреді. Нитроқосылыстарды сұйық фазада катализдік тотықсыздандырғанда процесс төмен температурада жүретіндіктен энергия жұмсалуды мен жүйенің қопарылғыштық қауіпсіздігі төмендейді. Аминді осы әдіспен синтездеу мақсатты өнімнің экологиялық таза және шығымы жоғары болады. Мақалада сутектің атмосфералық және жоғары қысымда нитроқосылыстарды гидрлеу үшін катализаторды таңдаудың барлық мәселелері толық жазылған. Өртүрлі тасымалдағыштарға (оның ішінде наноалмазда бар) қондырылған палладий, платина, родий негізіндегі катализаторда ароматты нитроқосылыстарды гидрлеу мәселесі қарастырылған. Мыс қосылған қондырылған палладий катализаторы негізіндегі катализаторлар функционалды топ – нитротопты гидрленгенде, ал платина және родий қосындылары – нитробензолдағы нитротопты және ароматты сақинаны тотықсыздандыруда жоғары селективтілік көрсетті. Жұмыста наноалмазға қондырылған өлшемі 4-5 нм платина және палладий нанобөлшектері негізіндегі катализаторлар жұмсақ жағдайда нитроқосылыстарды сұйық фазада гидрлеу реакциясында жоғары белсенділік көрсеткені анықталды. Мақала тақырыбы ғылыми және қолданбалы тұрғыдан өте қызықты. Теориялық сұрақ бойынша адсорбция, молекуланың реакциялық қабілетін кванттық-химиялық тұрғыдан сипаттау, тотықсыздану механизмі, металдардың электрондық күйі, ароматты нитроқосылыстардың өзгеру процесінің химизмі және ароматты нитроқосылыстарды катализдік гидрлеудің практикалық мәселелері туралы авторлардың жазған мәліметтері өте өзекті. Мақала отандық және шетелдік әдебиеттерді талдау негізінде жазылған, сонымен бірге химиялық және химиялық-технологиялық мамандығында оқитын студенттерге, магистранттарға, докторанттарға, катализ саласындағы мамандарға пайдалы болуы мүмкін.

Түйін сөздер: ароматты нитроқосылыстар, катализдік тотықсыздандыру, ароматты аминдер, селективті катализ, сұйық фазада гидрлеу.

Л.Р. Сасыкова¹, Н.Е. Максимов¹, А.Е. Ержанов¹, М. С. Илмуратова¹, А.Т.Райысов¹,
Е.А. Аубакиров¹, Р.Н. Ажигулова¹, А.А. Батырбаева¹, С. Сендилвелан²

¹Факультет химии и химической технологии, Казахский национальный университет
им. аль-Фараби, Алматы, Казахстан;

²Department of Mechanical Engineering, DR.M.G.R. Educational
and Research Institute, University, Chennai, Tamilnadu, India

ЭФФЕКТИВНЫЕ КАТАЛИЗАТОРЫ ДЛЯ СЕЛЕКТИВНОГО ВОССТАНОВЛЕНИЯ АРОМАТИЧЕСКИХ МОНО- И ДИНИТРОСОЕДИНЕНИЙ

Аннотация. В данной статье рассматриваются вопросы каталитического восстановления ароматических нитросоединений для получения ценных промежуточных и конечных продуктов – ароматических аминов. Ароматические моно-, ди- и полиамины, благодаря их высокой реакционной способности, широко используются в производстве различных соединений: синтетических красителей различных оттенков (для фотографий, в лакокрасочной промышленности, для окрашивания натуральных и синтетических волокон), фотохимикатов, стабилизаторов топлива и получения присадок, смазочных масел, химических средств защиты растений, синтетических волокон, сорбентов, лекарственных средств и т.д. Наиболее важным способом получения аминов из нитросоединений является каталитическое восстановление водородом на катализаторах. Большой вклад в изучение каталитического восстановления нитросоединений внесли ученые из СССР, стран СНГ, России и Казахстана. В настоящее время в некоторых странах, включая СНГ, метод восстановления нитросоединений в растворителях является одним из основных способов получения аминов. Благодаря применению растворителей, процесс проводится в более мягких условиях, чем при паровом методе гидрирования. Использование жидкофазного каталитического восстановления нитросоединений позволяет проводить процесс при достаточно низких температурах, что приводит к значительному снижению энергозатрат и взрывоопасности системы. Этот способ синтеза аминов является более экологически чистым, целевые продукты реакции, амины образуются с достаточно высокими выходами. В статье подробно описаны вопросы выбора катализаторов для гидрирования нитросоединений при атмосферном и повышенном давлении водорода. Описываются исследования реакций гидрирования ароматических нитросоединений на никелевых, медных и железных катализаторах. Рассмотрено гидрирование ароматических нитросоединений на катализаторах на основе палладия, платины, родия, нанесенных на различные носители, включая наноалмазы. Катализаторы на основе нанесенных палладиевых катализаторов с добавками меди показали высокую селективность при гидрировании нитрогрупп в нитросоединениях с функциональными группами, а с добавками платины и родия – при восстановлении и нитрогрупп, и ароматического кольца в нитробензоле. В работах по применению наноалмазов было установлено, что катализаторы на основе наночастиц платины и палладия размером 4-5 нм, закрепленные на наноалмазах, имели высокую активность в реакциях жидкофазного гидрирования нитросоединений в мягких условиях. Тема статьи интересна и с научной, и прикладной точек зрения. Описанные авторами данные по теоретическим вопросам (адсорбция, квантово-химическое описание реакционной способности молекул, механизмы восстановления, электронное состояние металлов, химия процессов превращения ароматических нитросоединений) и практическим проблемам каталитического гидрирования ароматических нитросоединений являются весьма актуальными. Статья составлена на основе анализа отечественной и зарубежной литературы и может быть полезна специалистам в области катализа и студентам, докторантам, обучающимся по специальностям химического и химико-технологического профиля.

Ключевые слова: ароматические нитросоединения, каталитическое восстановление, ароматические амины, селективный катализ, жидкофазное гидрирование.

Information about authors

Larissa R. Sasykova, Prof. of the Department of Physical Chemistry, Catalysis and Petrochemistry, Faculty of Chemistry and Chemical Technology, al-Farabi KazNU, larissa.rav@mail.ru, <https://orcid.org/0000-0003-4721-9758>;

Nariman E. Maximov, a first-year student of magistracy (specialty “Petrochemistry”) of the Department of Physical Chemistry, Catalysis and Petrochemistry, Faculty of Chemistry and Chemical Technology, al-Farabi KazNU, narimaksimov@gmail.com, <https://orcid.org/0000-0003-1337-1305>;

Arman Y. Yerzhanov, a first-year student of magistracy (specialty “Petrochemistry”) of the Department of Physical Chemistry, Catalysis and Petrochemistry, Faculty of Chemistry and Chemical Technology, al-Farabi KazNU, arman689396@gmail.com, <https://orcid.org/0000-0002-7856-3765>;

Madina S. Ilmuratova, a first-year student of magistracy (specialty “Petrochemistry”) of the Department of Physical Chemistry, Catalysis and Petrochemistry, Faculty of Chemistry and Chemical Technology, al-Farabi KazNU, ilmuratova97@mail.ru, <https://orcid.org/0000-0001-7773-6057>;

Abdolla T. Raiyssov, a first-year student of magistracy (specialty “Petrochemistry”) of the Department of Physical Chemistry, Catalysis and Petrochemistry, Faculty of Chemistry and Chemical Technology, al-Farabi KazNU, araiyssov2014@gmail.com, <https://orcid.org/0000-0002-4626-3346>;

Yermek A. Aubakirov, Prof., Head of the Department of Physical Chemistry, Catalysis and Petrochemistry, Faculty of Chemistry and Chemical Technology, al-Farabi KazNU, miral.64@mail.ru, <https://orcid.org/0000-0001-5405-4125>;

Ryskul N. Azhigulova, Ph.D., Ass. Prof. of the Department of Physical Chemistry, Catalysis and Petrochemistry, Faculty of Chemistry and Chemical Technology, al-Farabi KazNU, Almaty, Kazakhstan, razhigulova@gmail.com, <https://orcid.org/0000-0003-4498-8439>;

Aigul A. Batyrbaeva, Ph.D., Ass. Prof. of the Department of Physical Chemistry, Catalysis and Petrochemistry, Faculty of Chemistry and Chemical Technology, al-Farabi KazNU, Almaty, Kazakhstan, batyrbaeva_aigul@mail.ru, <https://orcid.org/0000-0003-2280-4846>;

Subramanian Sendilvelan, Prof., Dean, Department of Mechanical Engineering, Dr.Sc. M.G.R Educational and Research Institute, University, Chennai, India (Hirsch index 15), sendilvelan63@gmail.com, <https://orcid.org/0000-0003-1743-4246>

REFERENCES

- [1] <https://ru.wikipedia.org/wiki/Nitrosoyedineniya> (In Russ.).
- [2] Sassykova L.R., Sendilvelan S., Otzhan U., Vassilina G.K., Zhumakanova A.S., Mataeva Z.T., Amangeldi M.B. (2018) Theoretical and experimental researches of catalytic reduction of aromatic nitro compounds by molecular hydrogen in liquid phase, News of the National Academy of Sciences of the Republic of Kazakhstan, series of geology and technical sciences, 428(2):18-28. <https://doi.org/10.32014/2018.2518-170X.00> (In Eng.).
- [3] Aubakirov Y.A., Sassykova L.R. (2018) Selective catalytic reduction of aromatic nitro compounds and hydrocarbons, Almaty, Qazaq university, 338 p. ISBN 978-601-04-3441-7 (In Eng.).
- [4] Berkman B.E. (1964) Promyshlennyy sintez aromatcheskikh nitrosoyedineniy i aminov, M.:Khimiya (In Russ.).
- [5] Sokol'skiy V.D. (1975) Katalizatory gidrogenizatsii. Alma-Ata: Nauka KazSSR, s. 7-20. (In Russ.).
- [6] Sokol'skiy D.V. (1962) Gidrirovaniye v rastvorakh. Alma-Ata: Izd. AN Kaz. SSR, 457 s. (In Russ.).
- [7] Shesterkina A.A., Shuvalova E.V., Kirichenko O.A., Strelkova A.A., Nissenbaum V.D., Kapustin G.I., Kustov L.M. (2017) Application of silica-supported Fe–Cu nanoparticles in the selective hydrogenation of p-dinitrobenzene to p-phenylenediamine, Russian Journal of Physical Chemistry A, 91(2):201-204. (In Eng.).
- [8] Sassykova L.R., Aubakirov Y.A., Sendilvelan S., Tashmukhambetova Zh. Kh., Zhakirova N.K., Faizullaeva M.F., Batyrbaeva A.A., Ryskaliyeva R.G., Tyussyupova B.B., Abildin T.S. (2019) Studying the Mechanisms of Nitro Compounds Reduction (A-Review), Oriental Journal of Chemistry, 35(1):22-38. <https://doi.org/10.13005/ojc/350103> (In Eng.).
- [9] Mikhailov E.A., Kosilov A.T. (2010) Atomic structure of Pd_n (4 ≤ n ≤ 15) nanoclusters, Physics of the Solid State, 52(2):426-430. (In Eng.).
- [10] Kalita B., Deka R.C. (2007) Stability of small Pd_n (n = 1–7) clusters on the basis of structural and electronic properties: A density functional approach, J. Chem. Phys., 127(24):244-306. (In Eng.).
- [11] Zhang W., Ge Q., Wang L. (2003) Structure effects on the energetic, electronic, and magnetic properties of palladium nanoparticles, J. Chem. Phys., 118(13):5793-5801. (In Eng.).
- [12] Vassiliev Yu., Bagotzsky V.S., Khazova O.A., Krasnova N.N., Sergeeva T.A., Bogdanovich V.B. (1981) General scheme of adsorption, electroreduction and catalytic hydrogenation of nitro-compounds on platinum. I. Kinetics and mechanism of adsorption, Elektrochim. Acta, 26(4):545-562. (In Eng.).
- [13] Sokol'skiy D.V. (1984) Mekhanizmy kataliticheskoy gidrogenizatsii i optimizatsiya katalizatorov gidrirovaniya, v kn.:Mekhanizm kataliza, ch. 1. Novosibirsk. Nauka, s. 87-101. (In Russ.).
- [14] Osipova Y., Kurunina G.M., Zorina G.I., Butov G.M. (2014) Gidrirovaniye N-nitrofenola na Pt katalizatorakh, nanesennykh na oksidy RZE itriyevoy gruppy, Sovremennyye naukoymkiye tekhnologii, 7(2):109. (In Russ.).
- [15] Kurunina G.M., Butov G.M., Bezbabnykh M.V. (2016) Izucheniye kinetiki gidrirovaniya nitrobenzola na 1 % Pt katalizatorakh, sodержashchikh Eu2O3 i Sm2O3, Uspekhi sovremennogo yestestvoznaniya, 2:28-31. (In Russ.).
- [16] Jiang H.Y., Zheng X.X. (2015) Phosphine-functionalized ionic liquid-stabilized rhodium nanoparticles for selective hydrogenation of aromatic compounds, Applied Catalysis A: General, 499:118-123. <https://doi.org/10.1016/j.apcata.2015.04.01>. (In Eng.).
- [17] Blaser H.W., Indolese A., Setnyder A., Steiner H., Studer M. (2001) Supported palladium catalysts for fine chemical synthesis, J. Mol. Catal., 173:3-18. (In Eng.).
- [18] Magdalinova N.A., Kalmykov P.A., Klyuev M.V. (2014) Hydrogenation catalysts based on platinum- and palladium-containing nanodiamonds, Russian Journal of General Chemistry, 84(1):33-39. (In Eng.).
- [19] Dolmatov V.Yu., Fujimura T. (2005) Physical and chemical problems of modification of detonation nanodiamond surface properties. In: «Synthesis, Properties and Applications of Ultrananocrystalline Diamond», Eds. D. M. Gruen et al., Springer, Netherlands, 217-230. (In Eng.).
- [20] Kachevskii S.A., Golubina E.V., Lokteva E.S., Lunin V.V. (2007) Palladium on ultradisperse diamond and activated carbon: The relation between structure and activity in hydrodechlorination, Rus. J. Phys. Chem. A, 81(6):866-873. (In Eng.).

Publication Ethics and Publication Malpractice in the journals of the National Academy of Sciences of the Republic of Kazakhstan

For information on Ethics in publishing and Ethical guidelines for journal publication see <http://www.elsevier.com/publishingethics> and <http://www.elsevier.com/journal-authors/ethics>.

Submission of an article to the National Academy of Sciences of the Republic of Kazakhstan implies that the described work has not been published previously (except in the form of an abstract or as part of a published lecture or academic thesis or as an electronic preprint, see <http://www.elsevier.com/postingpolicy>), that it is not under consideration for publication elsewhere, that its publication is approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out, and that, if accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder. In particular, translations into English of papers already published in another language are not accepted.

No other forms of scientific misconduct are allowed, such as plagiarism, falsification, fraudulent data, incorrect interpretation of other works, incorrect citations, etc. The National Academy of Sciences of the Republic of Kazakhstan follows the Code of Conduct of the Committee on Publication Ethics (COPE), and follows the COPE Flowcharts for Resolving Cases of Suspected Misconduct (http://publicationethics.org/files/u2/New_Code.pdf). To verify originality, your article may be checked by the Cross Check originality detection service <http://www.elsevier.com/editors/plagdetect>.

The authors are obliged to participate in peer review process and be ready to provide corrections, clarifications, retractions and apologies when needed. All authors of a paper should have significantly contributed to the research.

The reviewers should provide objective judgments and should point out relevant published works which are not yet cited. Reviewed articles should be treated confidentially. The reviewers will be chosen in such a way that there is no conflict of interests with respect to the research, the authors and/or the research funders.

The editors have complete responsibility and authority to reject or accept a paper, and they will only accept a paper when reasonably certain. They will preserve anonymity of reviewers and promote publication of corrections, clarifications, retractions and apologies when needed. The acceptance of a paper automatically implies the copyright transfer to the National Academy of Sciences of the Republic of Kazakhstan.

The Editorial Board of the National Academy of Sciences of the Republic of Kazakhstan will monitor and safeguard publishing ethics.

Правила оформления статьи для публикации
в журнале смотреть на сайте:

www.nauka-nanrk.kz

<http://chemistry-technology.kz/index.php/en/arhiv>

ISSN 2518-1491 (Online), ISSN 2224-5286 (Print)

Редакторы: *М. С. Ахметова, Д. С. Аленов, А. Ахметова*
Верстка на компьютере *А.М. Кульгинбаевой*

Подписано в печать 06.09. 2020.
Формат 60x881/8. Бумага офсетная. Печать – ризограф.
9 п.л. Тираж 300. Заказ 4.