

ГОРЕНИЕ И ПЛАЗМОХИМИЯ

Том 17

1

2019

ГОРЕНИЕ И ПЛАЗМОХИМИЯ

**ЕЖЕКВАРТАЛЬНЫЙ ЖУРНАЛ НАУЧНОГО СОВЕТА ПО ГОРЕНИЮ И ВЗРЫВУ
ПРИ ПРЕЗИДИУМЕ РОССИЙСКОЙ АКАДЕМИИ НАУК И
ИНСТИТУТА ПРОБЛЕМ ГОРЕНИЯ МОН РК**

Издание рекомендовано ККСОН МОН РК

В журнале публикуются работы по фундаментальным и прикладным аспектам горения и плазмохимии, химической физики, наноматериалов и нанотехнологии

РЕДАКЦИОННАЯ КОЛЛЕГИЯ:

Главный редактор д.х.н. З.А. МАНСУРОВ
Зам. главного редактора д.т.н. А.Б. УСТИМЕНКО
Ответственный секретарь к.х.н. Д.У. БОДЫКОВ

ЧЛЕНЫ РЕДАКЦИОННОЙ КОЛЛЕГИИ

Р.Г. Абдулкаримова (Казахстан), В.В. Азатян (Россия), В.С. Арутюнов (Россия), И.Г. Ассовский (Россия), М.К. Атаманов (Казахстан), В.А. Бородуля (Белоруссия), В.И. Быков (Россия), Р. Бейсенов (Казахстан), А.А. Васильев (Россия), П.А. Власов (Россия), В.В. Голуб (Россия), В.Е. Зарко (Россия), З.Р. Исмагилов (Россия), А.Ж. Калтаев (Казахстан), Е.И. Карпенко (Россия), О.П. Коробейничев (Россия), Г.И. Ксандопуло (Казахстан), Ю.А. Лебедев (Россия), В.А. Левин (Россия), Ю.М. Максимов (Россия), А.А. Манташян (Армения), В.Е. Мессерле (Казахстан), Н.Н. Мофа (Казахстан), А.С. Мукасьян (США), М. Нажипкызы (Казахстан), Е.К. Онгарбаев (Казахстан), Г.Ш. Ониашвили (Грузия), Н.Г. Приходько (Казахстан), М.И. Тулепов (Казахстан), Б. Урмашев (Казахстан), С.М. Фролов (Россия), С.М. Фоменко (Казахстан), Н.М. Чикрадзе (Грузия), М.В. Чернышов (Россия), В.И. Юхвид (Россия)

Учредитель журнала:

РГП «Институт проблем горения» КН МОН РК

Научное издание

ISSN 1683-3902

ИБ № 67

Подписано в печать 15.06.2018. Формат 60x84 1/8. Бумага офсетная.

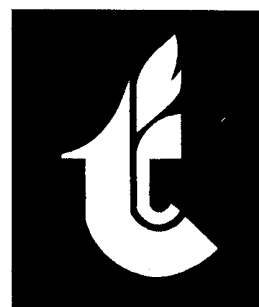
Печать цифровая. Объем 6,0 п.л. Заказ № 153. Тираж 15 экз.

Издательство «Қазақ университеті»

Казахского национального университета им. аль-Фараби.

050038 г. Алматы, пр. аль-Фараби, 71, КазНУ.

Отпечатано в типографии издательства «Қазақ университеті»



ГОРЕНИЕ И ПЛАЗМОХИМИЯ

Том 16

1

2019

*Журнал зарегистрирован в Агентстве Республики Казахстан по
связи и информации
Свидетельство о постановке на учет периодического печатного
издания № 14299-Ж от 18.04.2014 г.
Издается с 2003 г.*

*Решением Коллегии Комитета по надзору и аттестации в сфере
образования и науки МОН РК (Приказ № 376 на основании
протокола № 1 от 19.04.2016) научный журнал «Горение и
плазмохимия» включен в перечень изданий для публикации основных
научных результатов диссертаций по химическим и естественным
наукам*

Горение и плазмохимия. – Алматы: «Қазақ университеті», 2019. – 76 с.

Адрес редакции:

050012, г. Алматы, ул. Богенбай батыра, 172,

Институт проблем горения

<http://cpc.icp.kz/index.php/cpc>

Тел. +7 (727) 292-43-46, 267-51-41

Факс: +7 (727) 292-58-11

E-mail: **cpc-journal@icp.kz**

ГОРЕНИЕ И ПЛАЗМОХИМИЯ

ТОМ 17

№ 1

2019

СОДЕРЖАНИЕ

РАЗРАБОТКА И ИССЛЕДОВАНИЕ ГАЗОГЕНЕРИРУЮЩЕГО ПИРОТЕХНИЧЕСКОГО СОСТАВА НА
ОСНОВЕ УГЛЕВОДОРОДОВ

А.Т. Эбіш, Д.А. Байсейтов, Ш.Е. Габдрашова, М.И. Тулепов.3

CARBON BASED NANOCOMPOSITE MATERIAL FOR CO₂ CAPTURE TECHNOLOGY

A. Zhumagaliyeva, V. Gargiulo, F. Raganati, Z. Mansurov,
Ye. Doszhanov, M. Alfè. 9

PLASMA IGNITION OF DUST-COAL FLAME

V.E. Messerle, A.B. Ustimenko, K.A. Umbetkaliev 14

ТРЕХФАЗНЫЙ УНИВЕРСАЛЬНЫЙ ЭЛЕКТРОМАГНИТНЫЙ ТЕХНОЛОГИЧЕСКИЙ РЕАКТОР ДЛЯ
ПЕРЕРАБОТКИ МИНЕРАЛЬНЫХ ВЕЩЕСТВ

В.Г. Лукьященко, В.Е. Мессерле, А.Б. Устименко, С.Х. Акназаров,
К.А. Умбеткалиев.23

ВНУТРИСТРУКТУРНОЕ ТЕМПЕРАТУРНОЕ НАПРЯЖЕНИЕ – ОСНОВНОЙ
ФАКТОР РАЗРУШЕНИЯ ОГНЕУПОРОВ МЕТАЛЛУРГИЧЕСКИХ ПЕЧЕЙ

А.Х. Акишев, С.М. Фоменко, С. Төлендіұлы, Д.Т. Қашқынбай,
Н.Т. Рахым. 33

CONVERSION OF BIOETHANOL OVER OXIDE CATALYSTS

G.Y. Yergaziyeva, S. Tayrabekova, M. Mambetova,
S.Ozganbayeva, S.Smagulova. 40

ОКИСЛЕНИЕ ТЯЖЕЛЫХ НЕФТЯНЫХ ОСТАТКОВ В ПРИСУТСТВИИ
КАТАЛИЗАТОРОВ И МОДИФИКАТОРОВ

Е.К. Онгарбаев, А.Б. Жамболова, Е. Тилеуберди, Е.И. Иманбаев,
Е.А. Акказин, З.А. Мансуров47

CATALYSTS FOR HYDROCARBON HYDROGENATION PROCESSES

A.N. Aitugan, S.K. Tanirbergenova, Ye. Tileuberdi,
Ye.K. Ongarbayev, Z.A. Mansurov. 57

PREPARATION OF SILVER NANOPARTICLES WITH CONTROLLED
SIZE OF PARTICLES

K. Askaruly, S. Azat, A.R.Kerimkulova.65

СИНТЕЗ TiO₂ МЕТОДОМ ЭЛЕКТРОХИМИЧЕСКОГО АНОДИРОВАНИЯ

А.Н. Темиргалиева, М.А. Елеуов, Н.А. Мамытбеков, Б.Т.Лесбаев 73

CATALYSTS FOR HYDROCARBON HYDROGENATION PROCESSES

A.N. Aitugan¹, S.K. Tanirbergenova², Ye. Tileuberdi^{1,2}, Ye.K. Ongarbayev^{1,2}, Z.A. Mansurov^{1,2}

¹Al-Farabi Kazakh National University, al-Farabi ave. 71, Almaty, Kazakhstan

²Institute of Combustion Problems, Bogenbai batyr st. 172, Almaty, Kazakhstan

Received:
4 March 2019

Accepted:
28 March 2019

Available online:
6 May 2019

UDK 544.47

ABSTRACT

The article gives a review of the literature on the main groups of catalysts for the hydrogenation of hydrocarbons. The review describes the most actively studied hydrogenation catalysts in recent years, among which metal-modified catalysts on various supports occupy leading positions. Hydrogenation catalysts such as nickel catalysts on different carriers, nickel-chromium catalyst, catalysts on the basis of noble metals, including palladium, platinum, rhodium and ruthenium and methods of their preparation, structure, catalytic activity and the mechanism of action in processes of hydrogenation of unsaturated and aromatic compounds are considered. The use of different catalysts for the production of environmentally friendly motor fuels is considered. Specified features of the properties of catalysts are indicated depending on the method of preparation and composition. It is shown that the chemical technology and organic synthesis needs in competitive a product with smaller prime cost from local raw materials, the technology of creation of new, effective, ecologically acceptable catalysts for the account by need of the solution of a problem of receiving ecologically pure gasoline, without causing harm to the environmental environment is also demanded on the basis of the analysis of the existing catalysts of hydrogenation of unsaturated and aromatic hydrocarbons. Tasks are set for the researcher to create new approaches to solving existing economic and environmental problems associated with high energy costs and environmental pollution.

Keywords: catalysts, nanochemistry, hydrogenation, hydrocarbons, oil refining.

Introduction

Hydrogenation of hydrocarbons by C-C bond is one of the most important processes in organic synthesis, in the processing of petroleum products and in the production of environmentally friendly motor fuels that meet international standards. The process of hydrogenation of aromatic hydrocarbons is one of the main methods for the synthesis of cyclohexane, methyl cyclohexane and other alkyl naphthenes, besides this, hydrogenation of aromatic hydrocarbons can be used to dearomatize motor fuels. It is the practical importance of these processes. Interest for this process is constantly increasing due to the tightening of legislative requirements for the quality and composition of motor fuels. Metal-supported catalysts are used in this process

Currently, there are a number of different catalysts that are used as catalysts for the selective hydrogenation of hydrocarbons. These catalysts have properties such as increasing the surface of the active component, preventing sintering and saving expensive metal. Catalysts on the basis of nanoparticles of metals of platinum group - platinum, palladium, ruthenium

and rhodium are widely used in the processes of hydrogenation of hydrocarbons [1]. One of the main disadvantages of systems on the basis of metal particles is their sintering and aggregation leading to the gradual deactivation of the catalyst. To prevent agglomeration and sintering of active phase is deposited on various non-organic substrates - Al_2O_3 , SiO_2 , C, BaSO_4 , CaCO_3 [2]. There are also used copper, cobalt, nickel supported on various carriers for hydrogenation process except platinum group metals.

Nickel catalysts on different carriers

The deposited nickel catalysts are the most widely used for hydrogenation process, followed by catalysts on the basis of the noble metals. Nickel catalysts are capable of catalyzing the process of hydrogenation of olefins, cyclens and other unsaturated hydrocarbons and their derivatives. Hydrogenation of acetylenic compounds on iron catalysts proceeds, as a rule, selectively with the formation of compounds with a double bond. Selectivity of Co catalyst is lower, than iron catalyst. The hydrogenation of acetylene and their derivatives proceeds

easily on the nickel catalyst, but the selectivity is small.

The method of preparation of Ni catalysts includes the stages of impregnation, drying, dehydration, activation, restoration and passivation.

The following processes are used to prepare the precipitated and impregnating nickel catalysts:

1. Impregnation of the carrier (Al_2O_3 [3], SiO_2 [4], C and zeolites) with a salt solution, for example, nickel nitrate. After this, the catalyst is dried and pierced at a high temperature.

2. Mixing of precipitates active hydroxide $\text{Ni}(\text{OH})_2$ with a hydrogel carrier. Mixing continues 20-30 h. followed by extrusion, drying and piercing.

3. Applying sediment to another. For example, nickel hydroxide is precipitated by ammonia from a nickel nitrate solution in the presence of a suspension of hydrated aluminum oxide. The precipitate is filtered, rinsed thoroughly, dried and pierced at 500 °C for 2 hours in air.

4. Co-precipitation. The boiling solution of sodium silicate is slowly added to the solution of nickel salt. The precipitate is filtered, washed, dried and pierced.

It has been shown [5] that the adsorption and catalytic properties of nickel catalysts on the same carrier largely depend on the preparation method and on the reduction temperature. At high temperatures, the reduction leads to very active, but poison-sensitive catalysts; at low temperatures, it gives a less active and more stable contact. Catalysts with varying degree of reduction of nickel are obtained if temperature is changes and this affects to their activity. The efficiency of nickel catalysts on kieselguhr drops when obtaining a nickel catalyst from the original salts acetate> oxalate> nitrate. Upon receipt of nickel adsorption catalysts on synthetic aluminosilicate, their activity depends on the pH of the nickel salt solution. in the hydrogenation reaction.

Initially, metal catalysts were used in the hydrogenation of aromatic hydrocarbons: nickel, cobalt, copper, platinum and palladium, obtained by reduction of the corresponding oxides with hydrogen. Currently, among the catalysts for the hydrogenation of aromatic compounds, in particular aromatic hydrocarbons, Raney nickel, Adams platinum oxide, nickel, cobalt and platinum on various supports - activated carbon, aluminum oxide, silica gel, etc. - are best known.

Hydrogenation of benzene on nickel catalysts is carried out at low and middle pressure (to 3 MPa). So, Transformation of benzene into cyclohexane is reached at a temperature of 150-200 °C the almost complete, and in such conditions by-products are not formed. However in view of high sensitivity of nickel catalysts to impurity of sulfur, keeping of the last in initial benzene should not exceed ten thousand shares of percent; besides, express for contact purification of benzene is provided. Nickel catalysts on carriers are most often used: alumina, chromium oxide, etc.

Nickel nanoparticles supported on nanoferrite have been used as a catalyst for the hydrogenation of alkynes and ketones [6]. Hydrogenation was carried out in an autoclave at 10–15 atm H_2 and at room temperature for 48 hours or using isopropanol as a hydrogen donor at 100 °C with microwave radiation for 45 minutes.

Hydrogenation of various alkynes on nickel nanoparticles supported on nanomagnetite (Fe_3O_4) showed [6] that changing the solvent to dichloromethane leads to a change in the direction of the reaction: under the same conditions of hydrogenation, olefins are formed with yield 70–80 % in 48 hours.

Nickel-chromium catalyst

The nickel-chromium catalyst is also widely used for the hydrogenation of aromatic hydrocarbons (benzene) in the range of pressures of 2-6 MPa at 120-250 °C and the volumetric rate of benzene 0.5-2 hours. The catalyst is black shiny tablets (4x4 mm) with a bulk density of 1.1-1.3 g / ml and consists of metallic nickel or nickel black (at least 48 %) applied to chrome oxide (27 %). According to the author [7], the content of cyclohexane in hydrogenation under the above conditions is 99.9 %. The degree of conversion of benzene to cyclohexane varies depending on the height of the catalyst bed and on the duration of the hydrogenation.

Nickel catalysts are highly sensitive to the action of sulfur compounds. The withdrawal is associated with strong, irreducible adsorption of the latter, i.e. with the blocking of the active surface, at elevated temperatures and with the formation of chemical compounds. Hydrogen sulfide and sulfur containing organic compounds which are part of the original gas mixture, interacting with nickel, form nickel sulfide. In this case, the catalyst gradually loses activity. In most cases catalysts, repelled by sulfur compounds, do not regain their activity even when they switch to working with purified gas.

The amount of the poison suppressing a catalytic activity depends on dispersion of the fissile metal phase, and also on the content of metal in the catalyst. Than the surface of metal is more, especially nickel the chrome catalyst is steady. Therefore the precipitated catalyst containing about 50% of Ni is more resistant to effect of contact poisons, than nickel contacts on carriers.

Ability nickel the chrome catalyst to absorb sulfur give an opportunity to use it for thin purification of raw materials in conditions when hydrogenation of benzene proceeds in small degree (at 100-150 °C, atmospheric pressure and larger rates of volume flow). Endurance of the catalyst of hydrogenation consists about two years after cleaning of a feed stock.

That catalyst has rather low thermal resistance, its most admissible overheat 325-350 °C. Because the majority of heat is allocated in «front» catalyst beds, the catalyst is partially diluted with inert material for

decrease of its activity and prevention of overheat. Also the compounding thermostable nickel - aluminum and Ni-Al-Cr catalysts steady is offered at elevated temperatures.

Noble Metal Catalysts

Nickel-containing catalysts are cheaper than catalysts on the basis of noble metals (Pt, Pd, Ru, Rh, etc.). However, in a number of industrial hydrogenation processes, preference is given to the latter. This is due to their high catalytic activity, allowing the use of lower temperatures and pressures. The lifespan of such catalysts is often calculated in years. Pd-, Pt-, Ru- and Rh-catalysts on carriers and bimetal system have particular interest. The use of special carriers made it possible to reduce the content of noble metals to 0.01–0.005 % and thereby reduce the cost of the catalyst, retaining its quality [8].

The use of modern physicochemical research methods makes it possible to study the mechanism of action of these catalysts, to optimize their compositions using different carriers and modifiers, to develop ways to control the dispersity of metal on the surface of the carrier. Some catalysts on the basis of noble metals are resistant to degradation by S- and N-containing compounds [9].

The main metals used in the hydrogenation of alkynes are the metals of the platinum group, i.e. palladium, platinum, rhodium, ruthenium, iridium, nickel. Comparison of the catalytic activity and selectivity with respect to the olefin of various metals deposited on the Al_2O_3 substrate was carried out in [10] on the example of selective hydrogenation of acetylene at 50–150 °C and pressure of H_2 1–5 atm. The selectivity of this process is determined by two factors: the rate of hydrogenation of acetylene to ethylene or to the final alkane (kinetic factor) and competitive adsorption of acetylene and ethylene (thermodynamic factor). It was found that the selectivity of catalysts for ethylene decreased in the series: $\text{Pd} \gg \text{Rh} > \text{Pt} > \text{Ru} \gg \text{Ir}$.

In [11] studies, the effects of both metal and substrate on the selectivity of catalysts in the hydrogenation of alkyne at room temperature were studied simultaneously. It was found that the use of Pd nanoparticles (1 %) deposited on a SiO_2 substrate, as opposed to an Al_2O_3 substrate, at a substrate: $\text{H}_2 = 1:1$ ratio made it possible to obtain 100% of the expected product (100 % selectivity), while in the case of Pt nanoparticles (1 %), a backward dependence was observed. This can be explained by the different acidity of the substrate, and also by the effect of the particle size of the metals. High selectivity was demonstrated by samples with larger particles: 9 nm (Pd) and 7.8 nm (Pt), in contrast to particles of a smaller size (4.3 nm (Pd) and 3 nm (Pt), the use of which only led to a selectivity of 50 %. At this excess of hydrogen sharply

reduced the catalyst selectivity (up to 50 % propene). The catalyst's selectivity of 0.52 % Pt / SiO_2 increased with an increase in the substrate: H_2 ratio to 2.5: 1 while reducing the conversion to 20% [12]. The optimal ratio of substrates: H_2 was 1:1 in hydrogenation reaction at high temperatures (up to 150 °C).

Hydrogenation proceeds faster if the substrate contains a terminal triple bond, however, the catalyst manifests in this case, as a rule, less selectivity [13]. Hydrogenation of interior alkynes usually results in the predominant formation of cis-alkenes, which is associated with the synadsorption of the substrate and the successive addition of two adsorbed hydrogen atoms under the axis of the triple bond.

Palladium nanoparticles applied to organophilic montmorillonite by means of cation exchange in the interlayer space showed less activity and selectivity than $\text{Pd}_{77}\text{Ge}_{23}$. The optimal size of nanoparticles was 3.0 nm.

The presence of a benzene ring conjugated with a triple $\text{C}\equiv\text{C}$ bond significantly impedes the process of selective hydrogenation of aromatic alkynes.

Catalysts based on palladium

Palladium catalysts using the traditional method of water impregnation and impregnation in supercritical CO_2 (SC- CO_2) were synthesized to hydrogenation acetylene to ethane-ethylene fraction (EEF). It is established that the catalysts obtained in the SC - CO_2 environment have a higher selectivity for ethylene as compared with the catalysts obtained by water impregnation. The selectivity for ethylene with acetylene conversion equal to 100 % decreases with an increasing palladium content in the composition of the catalyst at the same time [14].

It was tested the influence both metal and support on the selectivity of catalyst for hydrogenation of alkynes at room temperature [11]. It was revealed that use of nanoparticles of Pd (1%) applied on SiO_2 support at a ratio substrate: $\text{H}_2 = 1:1$ in contrast with Al_2O_3 -support allowed to receive 100 % the expected product (selectivity of 100 %), in that time as in a case of nanoparticles of Pt (1 %) the return dependence was observed. It can be explained with various acidity of substrate, also influence of the size of particles of metals. The high selectivity was shown by exemplars with larger particles: 9 nanometers (Pd) and 7.8 nanometers (Pt), in difference from particles of the smaller size (4.3 nanometers (Pd) and 3 nanometers (Pt) which use resulted 50 % only in selectivity. Thus the excess of hydrogen sharply reduced selectivity of the catalyst (to 50 % propene). So, the selectivity of the catalyst of 0.52 % of Pt/ SiO_2 increased with increase in a ratio substrate: H_2 to 2.5:1 at simultaneous decrease of conversion up to 20 % [12]. Optimum ratio substrate was 1:1 H_2 at

reaction of hydrogenation at high temperatures (to 150 °C).

The palladium nanoparticles applied on organophilic montmorillonite by means of cationic exchange in interlayer space showed smaller activity and selectivity, than Pd₇₇Ge₂₃. The optimum size of nanoparticles was 3.0 nanometers.

Pd catalyst as a rule shows high selectivity on the relation to aromatic alkenes. So, for example, the modified Lindlar catalyst (Pd/CaCO₃/PEG/hinolin) selectively hydrogenates 1,2-bis(phenyl)ethyne to cis-stilbene with an atmospheric pressure and at room temperature to the current of one hour, it should be noted that the selectivity didn't fall lower than 90 % even at fivefold use of the catalyst [15].

Hydrogenation of cyclohexene and styrene was studied also in the presence of palladium nanoparticles by the sizes of 2-8 nanometers applied on nano-dimensional flakes of montmorillonite. Hydrogen at ambient temperature and atmospheric pressure is used for process [16]. Aluminum hydroxide used as a substrate for nanoparticles of palladium [16].

The selectivity of reaction of hydrogenation of propyne at 1 atm pressure and 25 °C temperature on the nanoparticles of palladium applied on particles of the poly(acrylic acid) was studied in work [17]. Nanoparticles with a size of several nanometers are obtained by restoring palladium acetate with sodium borohydride or lithium aluminum hydride. Conversion of propyne is reached 55-83 % at selectivity of hydrogenation in a propylene to 92 % in experiments.

The selection hydrogenation of acetylene in ethylene on bimetallic particles from Pd core and a silver cover is studied in work [18].

The palladium nanoparticles applied on polystyrene-polyethylene glycol copolymer catalyze not only hydrogenation of alkenes, but also the recovery dehalogenation of halogenarenes [18]. Derivatives of styrene, indene and cinnamic acid were taken as the alkenes, which was used as substrates in hydrogenation reaction derivatives of styrene, indene and cinnamyl acid. Process proceeded in an aqueous medium when heating reactionary weight at 25 °C and atmospheric pressure of hydrogen within 24 hours, yields of alkylbenzene made 97-99 %. Hydrodehalogenation of derivatives of benzene chloride, naphthalene chloride and chlorpyridine was carried out with using ammonium formate in a water isopropanol at 25 °C within 2 hours. Yields of products of dehalogenation made 85-99 %.

In work [19] the possibility of hydrogenation of acetylene and ethylene in ethane is shown by at a catalysis the silver and palladium nanoparticles applied on aluminum foil. Decrease in catalytic activity at increase in a share of atoms of silver in particles is revealed that is followed by increase in selectivity of hydrogenation of acetylene in ethylene.

Catalysts on a basis of noble metals are more active

and get poisoned with sulphurous connections less. The platinum and palladium applied on Al₂O₃ easily are deactivated at concentration of sulfur less than 1*10⁻⁴ %, however they are most sensitive to coke growth when using such acid carriers as zeolites [14].

Platinum catalysts for hydrogenation process

In the hydrogenation of aromatic acetylenes, catalysts on palladium, platinum, ruthenium and nickel are used.

Hydrogenation of benzene proceeds under the same conditions on platinum catalysts, as on nickel (temperature 150-250 °C, pressure to 3 MPa, a molar ratio gas: benzene = 8:1), and is reached the almost complete conversion at selectivity, the close to 100 %.

Platinum catalysts receive ionic exchange or impregnation of the carrier of solution of salt of Pt(NH₃)₄Cl₂; the last contacts the acid center of zeolite ≡Al-O-. Further the important stage of formation of centers 2 (≡Al-O-)...Pt₂ which is formed at an incideration on air with the subsequent reduction of hydrogens. Thus platinum is included into structure of clusters like m(≡Al-O-H) ... Pt_n. Clusters are in close contact with the strong acid centers that does possible transition of electrons from noble metal and leads to formation electron-deficient particles of metal (Pt^δ) defining special properties of the catalyst.

The platinum catalyst containing 0.3 % of Pt for aluminium is prepared by impregnation of granules of the carrier (3x3 mm) an aqueous solution of chloroplatinic acid with followed by drying and calcination; surface of the carrier 120 of m/g, m²/g platinum 0.25. Bulk weight of the catalyst is about 1 g/ml. The catalyst shouldn't contain chlorine and fluorine which promote reactions of an isomerization [20].

Hydrogenation of benzene was studied on nanoparticles of platinum of various form. The dependence of selectivity of reaction on a form of particles is found: there are obtained only cyclohexane on cubic particles, while on platinum cuboctahedra a mixture of cyclohexane and cyclohexene was formed [21]. It is found that activation energy of formation of cyclohexane in first case made 10.9 ± 0.4 kcal/mol, and at formation the mixture of cyclohexane and cyclohexene in the second case – 8.3 ± 0.2 and 12.2 ± 0.4 kcal/mol respectively. Exhaustive hydrogenation of aromatic hydrocarbons at atmospheric pressure of hydrogen and 60°C is carried out with use as the catalyst of nanothreads of platinum.

The advantages of platinum catalysts are necessary to carry them a little smaller sensitivity to sulfur compounds and a possibility of reactivation of the catalyst, than at nickel. The disadvantages are sensitivity to presence of moisture at raw materials that causes the necessity carefully to drain benzene.

Poisoning of platinum catalysts with compounds of sulfur is reversibly, unlike nickel contacts. Compounds of sulfur are hydrogenated to a hydrogen sulfide which interacts with platinum on reaction:



Bimetallic catalysts on carriers have a great interest during creation sulfur resistant hydrogenation catalysts on the basis of noble metals great interest. For example, it is known [21] that the combination of Pt and Pd applied on zeolite rises sulfur stability and an optimum ratio of Pt: Pd=1. Zeolite like Y with high relation of Si/Al, an also mordenity, borosilikaty, Y-and β -tseolita are used as a carrier.

Nanosized ruthenium catalysts

Examples of the selection hydrogenation of benzene to cyclohexane are known. For example, the colloid ruthenium catalyst (4 nm) applied on a silica gel at 40-60 atm and 140 °C catalyzes this reaction, and the selectivity on cyclohexane was from 80-90 % at small extents of conversion up to 40-50 % at 80-90 % of conversion of benzene [22].

Nanoparticles of ruthenium dioxide of 2-3 nanometers in size received by restitution of RuCl_3 sodium borohydride in ionic liquid [23] were used for hydrogenation of olefins and arenes. Hydrogenation was carried out in a two-phase system an alkene (arene) ionic liquid at 75 °C and 4 atm of H_2 , conversion of hexene-1, cyclohexane, 2,3-dimethyl-2-butene reached 99%, benzene, toluene and a p-xylol 64–97 %. Resultants of reaction were the corresponding alkanes and cycloalkanes.

The ruthenium nanoparticles applied on methylated cyclodextrins showed high catalytic activity at hydrogenation of olefins and aromatic hydrocarbons [23].

The ruthenium nanoparticles immobilized on SBA-15 silica gel in the presence of the ionic liquid prepared from 1,1,3,3 tetramethyl guanidines and lactic acid, also catalyze the quantitative hydrogenation of benzene in cyclohexane at 20 °C and atmospheric pressure of hydrogen [24]. The effectiveness of catalysis of hydrogenation of arenes with using of the stabilized colloidal solutions of nanoparticles of ruthenium is shown [24].

Ru-Pd-catalyst prepared by impregnation of the carrier salts of both metals have high activity. Na them hydrogenation of benzene was studied [25].

Catalysts based on rhodium

Comparison of catalytic activity of the nanoparticles of platinum, rhodium, palladium and gold applied on

carbon nanotubes in reaction of hydrogenation of aromatic hydrocarbons at atmospheric pressure of hydrogen is studied in work [26].

Really unique catalytic properties show nanoparticles of ruthenium, rhodium and iridium in reactions of hydrogenation of aromatic hydrocarbons. For example, the nanoparticles of iridium and rhodium of 2-4 nanometers in size applied on nanofibres of aluminum oxide allow hydrogenate benzene and an anisole in cyclohexane and methoxycyclohexane with the quantitative exit at ambient temperature and atmospheric pressure of hydrogen.

Influence of the stabilizing agents on catalytic activity of nanoparticles of rhodium at hydrogenation of cyclohexane showed that the major factor is the nature of interaction of the stabilizer with a surface of a particle [27]. The worst result was shown by application of a 1-oktadekaltiol (covalent binding); the intermediate activity was shown by the particles stabilized by poly(vinyl alcohol) (chemisorption); the best result is shown at application a tetraoctylammonium bromide (electrostatic interaction with the surface atoms). Thus, it is necessary to use the stabilizers of nanoparticles showing as much as possible weak chemical interaction with material of particles of the catalyst to increase in catalytic activity.

The study the impact of natural carrier as part of carbon catalysts to catalytic selectivity in the process of benzene hydrogenation are investigated [28]. It was described that the active and selective 1 % Rh zeolite catalyst for the hydrogenation process of benzene. 0.5% Rh-promoted clay-containing zeolite exhibits catalytic activity in the hydrogenation of benzene in the temperature range 280-350 °C, and also has high selectivity to output cyclohexane and DMB [29].

Less expensive materials also were used for hydrogenation of benzene in cyclohexane. In a particular, it is shown that the amorphous nanoparticles of Ni-Co-W-B received by restitution bord hydride of mix of salts of a cobalt, nickel and a tungstate of sodium [30] catalyze liquid-phase hydrogenation of benzene in the ethanol environment at 40 atm of H_2 and 100 °C in the steel autoclave when hashing.

Despite the existence of a wide range of known catalysts, chemical technology and organic synthesis are constantly in need of new, more efficient and environmentally acceptable catalysts. There are needed new approaches to solve the existing economic and environmental problems associated with high energy costs and environmental pollution in the development and improvement of industrial processes of basic and fine organic synthesis, as well as in petrochemistry, new approaches are needed to solve the existing economic and environmental problems associated with high energy costs and environmental pollution.

The creation of catalysts modified with metals is an effective way to change the properties of natural zeolite

to change its activity and selectivity in refining processes. Given the high cost of the developed catalysts, the Kazakhstan market needs a competitive product with lower costs from local raw materials. The technology to create new, efficient, environmentally acceptable catalysts is also in demand due to the need to solve the problem of obtaining environmentally friendly gasoline without harming the environment.

Conclusion

The review describes the most actively studied hydrogenation catalysts in recent years, among which metal-modified catalysts on various supports occupy leading positions.

Currently, the search of hydrogenation catalysts, deprived of deficiencies of sulphidised systems and having a low cost, is focused on nickel systems. Nickel catalysts are prone to rapid coking at elevated temperatures, but carrying out the process at low temperatures (150–250 °C) will lead to the dissolution of the nickel phase in the oil refining products, since oxidized nickel on the catalyst surface is not able to regenerate by itself at such temperatures. The researchers are faced with the task, on the one hand, of modifying the nickel catalyst with various components in order to decrease temperature of reduction of the nickel-containing phase to the temperature of the target reaction. On the other hand, it is required to stabilize the active nickel-containing component on the carrier with special approaches to the preparation of the catalyst and/or the including of stabilizing additives to improve the thermal stability of the catalyst. The main approach to achieve these requirements is to modify the nickel systems with the elements Cu, Mo, La, Co, Fe, B, P. At the same time, the researchers focus on the use of stable catalyst carriers or complete failure from them.

References

- [1]. Abu-Reziq, R.; Shenglof, M.; Penn, L.; Cohen, T.; Blum, J. Hydrogenation of arenes, alkenes and alkynes catalyzed by a sol-gel entrapped mixture of $[\text{Rh}(\text{COD})\text{Cl}]_2$ and $\text{Na}[\text{HRu}_3(\text{CO})_{11}]$. // *Journal of Molecular Catalysis A: Chemical*. - 2008. - V. 290. - № 1–2. - P. 30–34.
- [2]. Du, W.Q.; Rong, Z.M.; Liang, Y.; Wang, Y.; Lu, X.Y.; Wang, Y.F.; Lu, L.H. Chemoselective hydrogenation of unsaturated aldehydes with modified Pd/C catalyst. // *Chinese Chemical Letters*. - 2012. - V. 23. - № 7. - P. 773–776.
- [3]. Chen, J.; Liu, X.; Zhang, F. Composition regulation of bimetallic RuPd catalysts supported on porous alumina spheres for selective hydrogenation. // *Chemical Engineering Journal*. - 2015. - V. 259. - P. 43–52.
- [4]. Marín-Astorga, N.; Pecchi, G.; Fierro, J.L.G.; Reyes, P. A comparative study of Pd supported on MCM-41 and SiO_2 in the liquid phase hydrogenation of phenyl alkyl acetylenes mixtures. // *Journal of Molecular Catalysis A: Chemical*. - 2005. - V. 231. - № 1–2. - P. 67–74.
- [5]. Быкова М.В., Булавченко О.А., Ермаков Д.Ю., Лебедев М.Ю., Яковлев В.А., Пармон В.Н. // *Катализ в промышленности*. 2010. № 5. С.45
- [6]. Han Yuxiang, Peng Du, Xu Zhaoyi, Wan Haiqin, Zheng Shourong, Dongqiang Zhu. TiO_2 supported Pd@Ag as highly selective catalysts for hydrogenation of acetylene in excess ethylene // *Chem. Commun.* - V. 49. - 2013. - P. 8350–8352.
- [7]. Кричко А.А., Озеренко А.А., Фросин С.Б. и др. Получение и применение псевдогомогенных катализаторов для гидрогенизации и крекинга углеводородного сырья // *Катализ в нефтеперерабатывающей промышленности*. - 2018. - № 3. - С. 23–32.
- [8]. Song C., Ma X. Ultra-clean diesel fuels by deep desulphurization and deep dearomatization of middle distillates *Practical Advances of Petroleum Processing*. - 2006. - Vol. 2, - P. 317–347.
- [9]. Size-controlled synthesis of nickel nanoparticles / Y. Hou [et al] // *Applied Surface Science*. - 2017. - V. 241. - P. 218 - 222.
- [10]. Platinum Nanoparticle Shape Effects on Benzene Hydrogenation Selectivity / K. M. Bratlie [et al] // *Nano Letters*. - 2017. - V. 7. - P. 3097–3101.
- [11]. Bond, G.C.; Wells, P.B. Hydrogenation of the acetylene. III. Reaction of acetylene with hydrogen catalysed by alumina-supported rhodium and iridium. // *J. Catal.* - 1966. - V. 5. - № 3. - P. 419–427.
- [12]. Kennedy, D.R.; Webb, G.; Jackson, S.D.; Lennon, D. Propyne hydrogenation over aluminasupported palladium and platinum catalysts. // *Applied Catalysis A: General*. - 2004. - V. 259. - P. 109–210.
- [13]. Garcia, P.E.; Lynch, A.S.; Monaghan, A.; Jackson, S.D. Using modifiers to specify stereochemistry and enhance selectivity and activity in palladium-catalysed, liquid phase hydrogenation of alkynes. // *Catalysis Today*. - 2011. - V. 164. - P. 548–551.
- [14]. Mastalir, Á.; Király, Z.; Berger, F. Comparative study of size-quantized Pd-montmorillonite catalysts in liquid-phase semi-hydrogenations of alkynes. // *Applied Catalysis A: General*. 2004. - V. 269. - P. 161–168.
- [15]. Kacer, P.; Kuzma, M.; Cervený, L. The molecular structure effects in hydrogenation of cycloalkyl substituted alkynes and alkenes on platinum and palladium catalysts. // *Applied Catalysis A: General*. - 2004. - V. 259. - P. 179–183.
- [16]. Chandrasekhar, S.; Narsihmulu, Ch.; Chandrasekhar, G.; Shyamsunder, T. Pd/ CaCO_3 in liquid poly(ethylene glycol) (PEG): an easy and efficient recycle for partial reduction of alkynes to cis-olefins under a hydrogen atmosphere. // *Tetrahedron Letters*. - 2004. - V. 45. - P. 2421–2423.
- [17]. Selektivnoe gidrirovanie fenilacetilena v stirol na nanochastitsakh zolota / S. A. Nikolaev, N. A. Permyakov, V. V. Smirnov, A. Yu. Vasil'kov, S. N. Lanin // *Kinetika i kataliz*. - 2010. - V. 51, № 2. - P. 305–309.
- [18]. In Soo Park, Min Serk Kwon, Kyung Yeon Kang, Jae Sung Lee, Jaiwook Park. Rhodium and Iridium Nanoparticles Entrapped in Aluminum Oxyhydroxide Nanofibers: Catalysts for Hydrogenations of Arenes and Ketones

- at Room Temperature with Hydrogen Balloon // *Adv. Synth. Catal.* – V. 349. – 2007. – P. 2039–2047.
- [19]. Antal Sárkány. Acetylene Hydrogenation on SiO₂ Supported Gold Nanoparticles // *React. Kinet. Catal. Lett.* – V. 96. – № 1. – 2009. – P. 43–54.
- [20]. Catalytic Consequences of Particle Size and Chloride Promotion in the Ring Opening of Cyclopentane on Pt/Al₂O₃ / H. Shi [et al] // *ACS Catalysis.* – 2018. – V. 3. – P. 328–338.
- [21]. Yu Tingting, Wang Jiaqing, Li Xinming, Cao Xueqin, Gu Hongwei. An Improved Method for the Complete Hydrogenation of Aromatic Compounds under 1 Bar H₂ with Platinum Nanowires // *Chem. Cat. Chem.* – V. 5. – 2013. – P. 2852–2855.
- [22]. Niu, M.; Wang, Y.; Li, W.; Jiang, J.; Jin, Z. Highly efficient and recyclable ruthenium nanoparticle catalyst for semihydrogenation of alkynes. // *Catalysis Communications.* – 2013. – V. 38. – P. 77–81.
- [23]. Denicourt-Nowicki A., Ponchel A., Monflier E., Rou-coux A. Methylated cyclodextrins: an efficient protective agent in water for zerovalent ruthenium nanoparticles and a supramolecular shuttle in alkene and arene hydrogenation reactions // *Dalton Trans.* – V. 12. – 2007. – P. 5714–5719.
- [24]. Byunghoon Yoon, Horng-Bin Pan, and Chien M. Wai. Relative Catalytic Activities of Carbon Nanotube-Supported Metallic Nanoparticles for Room-Temperature Hydrogenation of Benzene // *J. Phys. Chem. C.* – V. 113. – № 4. – 2009. – P. 1137–1640.
- [25]. Riley, C., De La Riva, A., Zhou, S., Wan, Q., Peterson, E., Artyushkova, K., ... Datye, A. (2019). Synthesis of Nickel-Doped Ceria Catalysts for Selective Acetylene Hydrogenation. *ChemCatChem*. doi:10.1002/cctc.201801976
- [26]. Selektivnoe gidrirovaniye s ispol'zovaniem nanokatalizatorov / S. V. Levanova // *Zhurnal Prikladnoj Khimii.* – 2009. – V. 82, № 5. – P. 830–833. [in Russian]
- [27]. Roucoux, A., Schulz J., Patin H. Arene Hydrogenation with a Stabilised Aqueous Rhodium (0) Suspension: A Major Effect of the Surfactant Counter-Anion // *Advanced Synthesis & Catalysis.* – V. 345. – № 1–2. – 2003. – P. 222–229
- [28]. A. Temirkhan, Z. A. Mansurov, S. K. Tanyrbergenova, N. K. Zhylybayeva, and G. M. Naurzbayeva, A. Aitugan. The impact of natural carrier as part of catalysts to catalytic selrctivity in benzene hydrogenation. IX Международный симпозиум «Физика и химия углеродных материалов/наноинженерия» Международная конференция «Наноэнергетические материалы и наноэнергетика». Алматы, Казахстан, 2016. С. 35-40.
- [29]. S. K. Tanyrbergenova, A. Temirkhan, Z. A. Mansurov, N. K. Zhylybayeva, and G. M. Naurzbayeva. Rh-promoted carbon catalysts to obtain clean components of motor fuels. *International journal of chemical engineering and applications.* Vol. 7. No.1. February, 2016. P. 11-16.
- [30]. Ultrafine Ni-Co-W-B amorphous alloys and their activities in benzene hydrogenation to cyclohexane / M.-H. Qiao [et al] // *Catalysis Letters.* – 2001. – V. 71. – P. 187–192.

Катализаторы для процессов гидрирования углеводородов

А.Н. Айтуган¹, С.К. Танирбергенова^{1,2},
Е. Тилеуберди^{1,2}, Е.К. Онгарбаев^{1,2}, З.А. Мансуров^{1,2}

¹Казахский Национальный Университет имени Аль-Фараби, Алматы, Казахстан

²Институт проблем горения, Алматы, Казахстан

АННОТАЦИЯ

В статье приводится обзор литературы по основным группам катализаторов для гидрирования углеводородов. В обзоре рассмотрены наиболее активно изучаемые в последние годы катализаторы гидрирования, к числу которых относятся металлические модифицированные катализаторы на разных носителях. Рассмотрены катализаторы гидрирования такие, как никелевые катализаторы на разных носителях, никель-хромовый катализатор, катализаторы на основе благородных металлов, в том числе палладий, платина, родий и рутений и методы их приготовления, структура, каталитическая активность и механизм действия в процессах гидрирования непредельных и ароматических соединений. Рассматривается использование разных катализаторов для получения экологических чистых моторных топлив. Указаны особенности свойств катализаторов в зависимости от способа приготовления и состава. На основе анализа существующих катализаторов гидрирования непредельных и ароматических углеводородов показано что химическая технология и органический синтез нуждается в конкурентоспособным продукте с меньшей себестоимостью из местного сырья, так же востребована технология создания новых, эффективных, экологически приемлемых катализаторов за счет необходимостью решения проблемы получения экологически чистого бензина, без нанесения вреда окружающей среде. Поставлены задачи перед исследователем необходимости новых подходов к решению существующих экономических и экологических проблем, связанных с большими энергетическими затратами и загрязнением окружающей среды.

Ключевые слова: катализаторы, нанохимия, гидрирование, углеводороды, нефтепереработка.

Көмірсутектерді гидрлеу процессіне арналған катализаторлар

А.Н. Айтүған¹, С.Қ. Танирбергенова^{1,2}, Е. Тілеуберді^{1,2},
Е.К. Оңғарбаев^{1,2}, З.А. Мансуров^{1,2}

¹Әл-Фараби атындағы Қазақ Ұлттық Университеті, Алматы, Қазақстан

²Жану Проблемалары Институты, Алматы, Қазақстан

АННОТАЦИЯ

Мақалада көмірсутектерді гидрлеуге арналған катализаторлардың негізгі топтары бойынша әдебиеттік шолу келтірілген. Соңғы жылдарда белсенді зерттелген гидрлеу катализаторларын, атап айтқанда әр түрлі қондырғыштарға отырғызылған модифицирленген металл катализаторлары шолуда қарастырылған. Әр түрлі қондырғыштарға отырғызылған никель катализаторлары, никель-хром катализаторы, асыл металдар негізіндегі катализаторлар, соның ішінде паладий, платина, родий, рутений сияқты гидрлеу катализаторлары және оларды дайындау жолдары, құрылымы, каталитикалық активтілігі және қанықпаған және ароматты көмірсутектерді гидрлеу үрдісіндегі әрекет ету механизмі шолуда келтірілген. Экологиялық таза

мотор отындарын алуға арналған әр түрлі катализаторлардың пайдалануы қарастырылған. Катализатор қасиеттерінің оны дайындау әдісі мен құрамына тәуелділігі көрсетілген. Қолданыстағы қанықпаған және ароматты көмірсутектерді гидрлеу катализаторларын талдау негізінде химиялық технология мен органикалық синтез қоршаған ортаға зиянын тигізбейтін, экологиялық таза бензинді алу қажеттілігіне байланысты жаңа, эффективті және экологиялық тұрғыда тиімді катализатор жасап шығару технологиясы мен бәсекеге қабілетті, өзіндік құны төмен жергілікті шикізаттан жасалған өнімге мұқтаж екендігі көрсетілген. Зерттеуші алдына үлкен энергия шығындарымен және қоршаған ортаның ластануымен байланысты қазіргі экономикалық және экологиялық проблемаларды шешудің жаңа тәсілдерін жасау міндеті қойылған.

Түйін сөздер: катализаторлар, нанохимия, гидрлеу, көмірсутектер, мұнай өндеу.