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

ҚАЗАҚСТАН РЕСПУБЛИКАСЫ
ҰЛТТЫҚ ҒЫЛЫМ АКАДЕМИЯСЫНЫҢ

Д.В.СОКОЛЬСКИЙ АТЫНДАҒЫ «ЖАНАРМАЙ,
КАТАЛИЗ ЖӘНЕ ЭЛЕКТРОХИМИЯ ИНСТИТУТЫ» АҚ

ХАБАРЛАРЫ

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»

ХИМИЯ ЖӘНЕ ТЕХНОЛОГИЯ СЕРИЯСЫ

◆

СЕРИЯ ХИМИИ И ТЕХНОЛОГИИ

◆

SERIES CHEMISTRY AND TECHNOLOGY

6 (432)

ҚАРАША – ЖЕЛТОҚСАН 2018 ж.
НОЯБРЬ – ДЕКАБРЬ 2018 г.
NOVEMBER – DECEMBER 2018

1947 ЖЫЛДЫҢ ҚАҢТАР АЙЫНАН ШЫҒА БАСТАҒАН
ИЗДАЕТСЯ С ЯНВАРЯ 1947 ГОДА
PUBLISHED SINCE JANUARY 1947

ЖЫЛЫНА 6 РЕТ ШЫҒАДЫ
ВЫХОДИТ 6 РАЗ В ГОД
PUBLISHED 6 TIMES A YEAR

АЛМАТЫ, ҚР ҰҒА
АЛМАТЫ, НАН РК
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. Webof 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.

«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 Мәдениет пен ақпарат министрлігінің Ақпарат және мұрағат комитетінде 30.04.2010 ж. берілген **№1089-Ж** мерзімдік басылым тіркеуіне қойылу туралы куәлік

Мерзімділігі: жылына 6 рет.
Тиражы: 300 дана.

Редакцияның мекенжайы: 050010, Алматы қ., Шевченко көш., 28, 219 бөл., 220, тел.: 272-13-19, 272-13-18, www:nauka-nanrk.kz / chemistry-technology.kz

---

Типографияның мекенжайы: «Аруна» ЖК, Алматы қ., Муратбаева көш., 75.

«Известия НАН РК. Серия химии и технологии».
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 и архивов Министерства культуры и информации Республики Казахстан **№10893-Ж,** выданное 30.04.2010 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://nauka-nanrk.kz / chemistry-technology.kz

Адрес редакции: 050100, г. Алматы, ул. Кунаева, 142,
Институт органического катализа и электрохимии им. Д. В. Сокольского,
каб. 310, тел. 291-62-80, факс 291-57-22, e-mail:orgcat@nursat.kz
Адрес типографии: ИП «Аруна», г. Алматы, ул. Муратбаева, 75

N E W S
OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES CHEMISTRY AND TECHNOLOGY
ISSN 2224-5286 **https://doi.org/10.32014/2018.2518-1491.23**
Volume 6, Number 432 (2018), 29 – 37

UDC 541.128.13:542.975’973:541.64

E.T. Talgatov, A.S. Auyezkhanova, N.Z. Tumabayev,
S.N. Akhmetova, K.S. Seitkalieva, Y.A. Begmat, A.К. Zharmagambetova

D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry, Almaty, Kazakhstan
eldar-talgatov@mail.ru

POLYMER-PALLADIUM CATALYSTS ON MAGNETIC SUPPORT FOR HYDROGENATION OF PHENYLACETHYLENE

Abstract. Pd-polymer catalysts on magnetic support (MS) have been successfully prepared by adsorption method. The magnetic support was synthesized by co-precipitation of iron chlorides (Fe^{3+}:Fe^{2+} = 2:1) with sodium hydroxide. A series of colloidal palladium solutions was prepared by reduction of K_2PdCl_4 with sodium borohydride in the presence of polyacrylamide (PAM) and polyacrylic acid (PAA) with a different mole ratios of palladium to polymer (Pd:PAA = 1:5; Pd:PAM = 1:5; Pd:PAM = 1:10 and Pd:PAM = 1:15).

The initial components and catalysts were characterized by physicochemical methods. XRD measurement was used to identify the crystalline structure of the magnetic material. The results based on the crystal planes showed that the synthesized sample corresponds to maghemite with a spinal structure and an average particle size of 8.5 nm. The disappearance of the absorption band of $PdCl_4^{2-}$ ions at 425 nm indicated a complete reduction of palladium. According to elemental analysis, the content of palladium in the catalysts was 1wt.% of the sum of all components which was close to the calculated data. This result indicated the quantitative fixation of polymer-protected palladium particles to a magnetic support.

The developed catalysts showed rather high activity and selectivity in the hydrogenation of phenylacetylene to styrene ($W_{C\equiv C}$ = 0.73-1.36×10^{-6} mol/s, S_{st} = 80.9-89.2%). The PAM-stabilized catalysts were characterized by higher rate and yield of styrene to compare to the Pd-PAA/MS catalyst. The increase of the polymer content in the catalysts affects insignificantly the catalytic properties of the Pd-PAM/MS.

Keywords. Palladium, polymer, magnetic catalyst, hydrogenation, phenylacetylene.

Introduction

Recently, the interest of researchers of various fields of science and technology is focused on magnetic nanoparticles due to their unique properties as superparamagnetism, high coercivity, biocompatibility [1-3]. One of the promising areas of application of magnetic nanoparticles is design of catalysts. The uses of such nanoparticles as a support provides high effectiveness of disperse catalytic systems and the easiness of their separation from the reaction medium by magnetic field [4-5]. Platinum [6-8], palladium [9-11] and ruthenium [12, 13] are the most often used active phase of such type of catalysts.

Palladium magnetic catalysts exhibit high activity in cross-coupling reactions [14, 15] and hydrogenation of various classes of organic compounds [16-18]. However, despite a large number of methods for preparation of catalysts with magnetic properties [19-21], there are only few publications on optimization of their synthesis. The purpose of this work therefore is to develop palladium catalysts with magnetic properties, as well as to study the effects of the polymer-stabilizer nature and the ratio of Pd to polymer on catalytic properties of synthesized Pd-polymer/MS composites in the hydrogenation of phenylacetylene as model unsaturated hydrocarbon.

Experimental part

Reagents and materials

Phenylacetylene (98%, Aldrich) was purified by distillation, a purity was checked chromatographically. Ethanol (pure grade), $PdCl_2$ (59-60% Pd, Aldrich), KCl (pure grade), $FeCl_2{\cdot}4H_2O$ (pure grade), $FeCl_3{\cdot}6H_2O$ (pure grade), $NaBH_4$ (96%, Aldrich), NaOH (pure grade), polyacrylamide (PAM, M_w = 1000000) and polyacrylic acid (PAA, M_v = 1250000, Aldrich) were used without additional purification.

Synthesis of magnetic support (MS)

The iron salts ($FeCl_3{\cdot}6H_2O$ -21.6 g and $FeCl_2{\cdot}4H_2O$ - 8.0 g) were dissolved in 200 mL of pre-boiled distilled water at room temperature, and placed to a thermostated round-bottom flask with three outlets and heated to 40°C. Then 100 mL of 3.2 M sodium hydroxide solution was added to the flask, stirred by bubbling nitrogen during 1 hour and then cooled to room temperature. The resulting black precipitate was separated from the supernatant by magnetic separation and washed several times with D.I. water and stored in ethanol.

The crystallinity of the prepared magnetite sample was studied by X-ray diffractometer DRON 3 with cobalt Kα radiation (λ = 0.179 nm).

Synthesis of polymer-protected Pd nanoparticles

Freshly prepared aqueous solution of $NaBH_4$ (10 mL of 0.05 mmol, 1.9 mg) was rapidly added to 90 mL of an aqueous mixture of K_2PdCl_4 (0.1 mmol, 10.6 mgPd) and a polymer (0.5-1.5 mmol, 36.0-108.5 mg) under vigorous magnetic stirring. The amount of polymer was taken based on the calculation for preparing polymer-protected palladium nanoparticles with a molar ratios of Pd:polymer = 1: 5; 1:10 and 1:15.

The degree of palladium reduction was evaluated spectrophotometerically (SF-2000, Russia) by disappearance of the absorption band of palladium ions at 425 nm

Catalysts preparation

Pd colloidal solutions and a magnetic support amounts were taken from the calculation for obtaining 1% Pd catalysts. Palladium fixation to the magnetic support was assessed visually by brightening the mother liquor. The content of palladium in the catalysts was determined on a X-ArtM COMITA X-ray fluorescence spectrometer.

The prepared colloidal palladium solution (100 mL of $1{\times}10^{-3}$ mol/L) was poured into 35 mL of ethanol suspension of the magnetic material (29 mg/mL). The mixture was stirred with a shaker for 30 minutes. The resulting catalyst was separated from the mother liquor by magnetic separation, washed with D.I. water and dried in the air.

Hydrogenation process

Hydrogenation of phenylacetylene (0.25 mL) was carried out in a thermostated glass reactor at 40 ° C and atmospheric hydrogen pressure in ethanol (25 mL) [22]. The catalyst amount was 0.02 g. The reaction rate was calculated based on the change in volume of uptaken hydrogen per second.

The reaction products were analyzed by gas chromatography on a Chromos GC-1000 chromatograph (Chromos, Russia) with the a flame ionization detector in the isothermal regime using a BP21 (FFAP) capillary column with a polar phase (PEG modified with nitroterephthalate) 50 m in length and 0.32 mm in inside diameter. The column temperature was 90°C, and the injector temperature was 200°C; helium served as the carrier gas; the injected sample volume was 0.2 μL. The selectivity of the catalyst was evaluated as the ratio of the targeting product to the sum of all reaction products at a fixed conversion.

Results and discussion

Analysis of initial components and catalysts

Figure 1 shown XRD patterns of the synthesized magnetic sample. Seven characteristic peaks at 2θ 21.564°, 35.297°, 41.629°, 50.600°, 63.595°, 67.540° and 74.556° were corresponding to the (111), (220), (311), (400), (422), (511) and (440) crystal planes of a maghemite with a spinal structure [23]. The average crystallite size calculated using the Debye-Scherrer equation was about 8.5 nm.

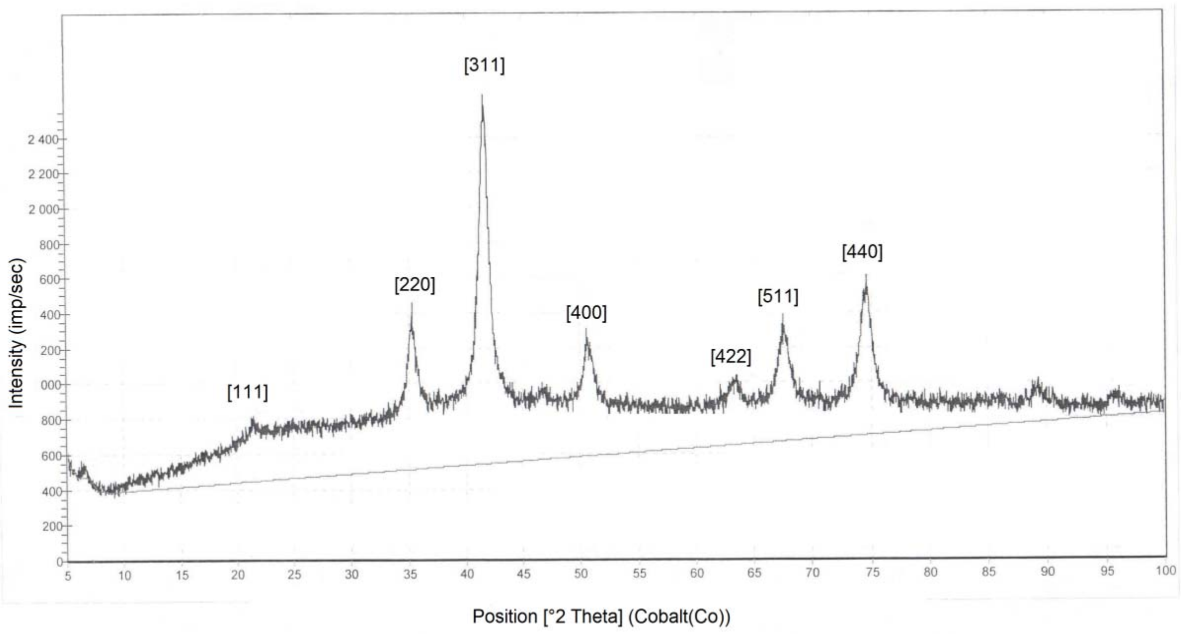


Figure 1 - X-ray diffraction pattern of the synthesized magnetic sample

According to spectrophotometric data, the addition of a reducing agent to a solution of palladium salt and a polymer leads to completely reduction of the metal ions at a ratio of Pd:$NaBH_4$ = 2:1. The disappearance of the absorption band of $PdCl_4^{2-}$ ions at 425 nm in the spectrum of the reduced sample has confirmed the transition of Pd^{2+} to the zerovalent state (Figure 2).

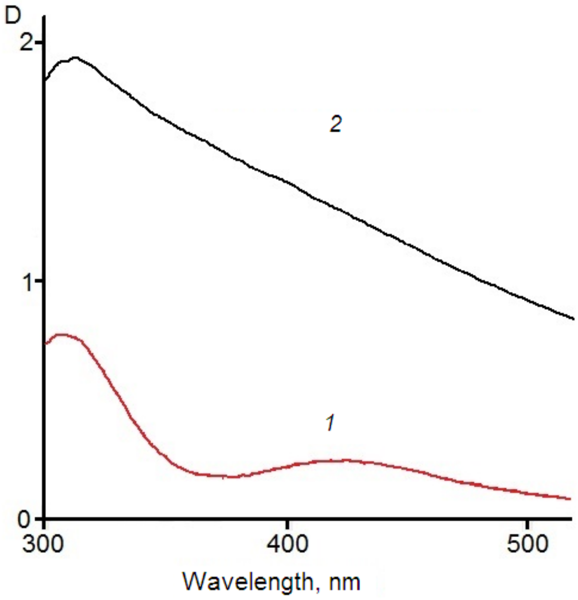


Figure 2 - The absorption spectrum of the palladium salt solution before (curve *1*) and after (curve *2*) metal reduction

The catalysts were prepared by adsorption of polymer-protected palladium particles onto the synthesized magnetic material. Clarity of the mother liquor after magnetic separation indicated the quantitative fixation of the metal-macromolecule active phase to the support (Figure 3). The active phase was probably fixed to support due to reducing the surface energy of the magnetic nanoparticles.

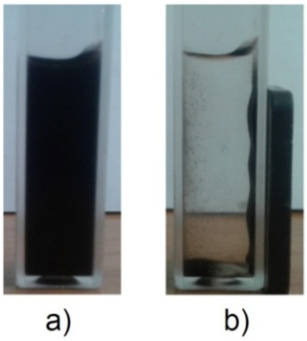


Figure 3 – Photos of the Pd-PAM(1:15) and MS mixture before (a) and after (b) magnetic separation

The complete Pd adsorption of on the magnetic sample was also confirmed by the results of the elemental analysis of the Pd-PAM(1:15)/MS catalyst (Table 1) in which the metal content was close to the calculated data and was 1wt.% of the sum of all components.

Table 1 – Elemental analysis data of the Pd-PAM(1:15)/MS catalyst

Element concentration, wt. %			
O	Cl	Fe	Pd
29.00	0.77	68.50	1.00

Catalytic properties of Pd-polymer/MS in phenylacetylene hydrogenation

Hydrogenation of phenylacetylene on 1% Pd-PAA(1:5)/MS in the first 70 minutes proceeds at a constant rate (0.7×10^{-6} mol/s) which in ~70 minutes insignificantly increased. The sharp slowing of the reaction begins at the 90th minute (Figure 4, curve *1*). The activity of 1% Pd-PAM(1:5)/MS catalyst is 1.3-1.7 times higher than that of the catalyst stabilized with polyacrylic acid, however, the kinetic curve form was similar (Figure 4, curve *2*).

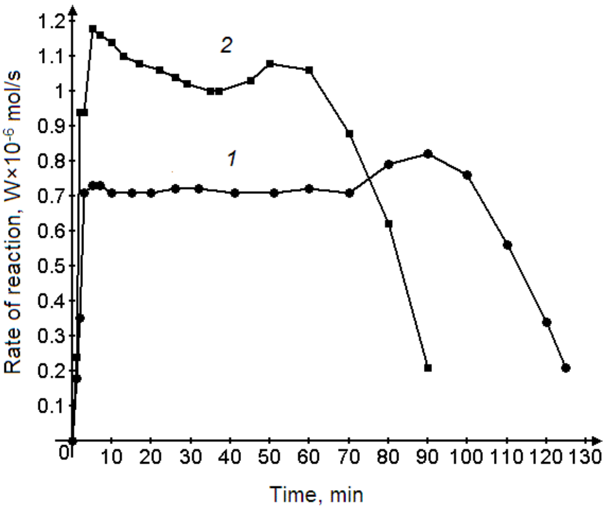
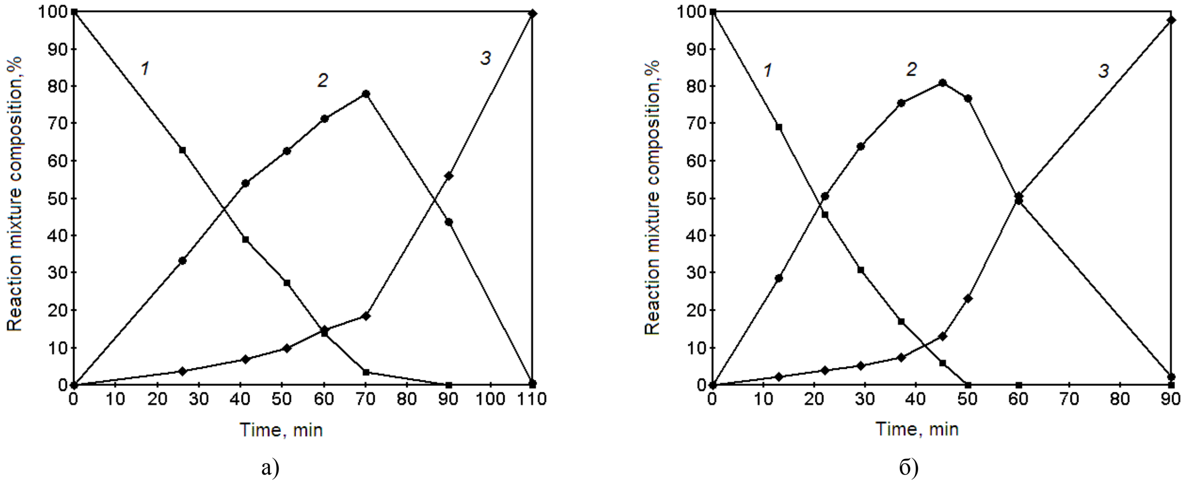


Figure 4 - Changes in the rate of phenylacetylene hydrogenation in the presence of (*1*) Pd-PAA(1:5)/MS and (*2*) Pd-PAM(1:5)/MS. Conditions: catalyst sample weight, 0.02 g; temperature, 40°C; H_2 pressure, 0.1 MPa; solvent, ethanol (25 mL); and initial phenylacetylene amount, 0.25 mL.

According to chromatographic analysis, a rapid increase in the styrene content occurred on Pd-PAA(1:5)/MS in the initial period of time. Then its amount decreased due to its reduction to ethylbenzene (Figure 5a). Similar changing the composition of the reaction products was observed during hydrogenation of phenylacetylene on Pd-PAM(1:5)/MS (Figure 5b). The maximum styrene content reached at 70th minute (78.1%) and at 45th minute (81.0%) on PAA- and PAM-stabilized catalysts, correspondingly. These time values coincide with the time of increase in the reaction rates on these catalysts (Figure 4, curves *1* and *2*)



а)

б)

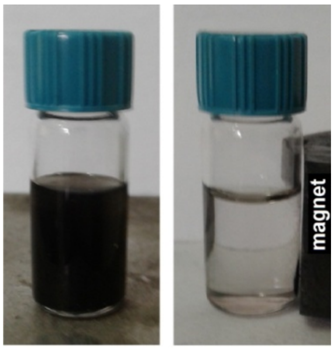
Figure 5 - Changes in the composition of reaction mixtures during of phenylacetylene hydrogenation on (a) Pd-PAA(1:5)/MS and (b) Pd-PAM(1:5)/MS: (1) phenylacetylene, (2) styrene, and (3) ethylbenzene. Conditions: catalyst sample weight, 0.02 g; temperature, 40°C; H_2 pressure, 0.1 MPa; solvent, ethanol (25 mL); and initial phenylacetylene amount, 0.25 mL.

The lower activity and selectivity of Pd-PAA(1:5)/MS (80.9%) compared with Pd-PAM(1:5)/MS catalyst (88.0%) (Table 2) was probably due to the stronger interaction of PAA with catalyst components [24], and, as a consequence, more difficult access of the substrate to palladium active centers.

Table 2 - Results of the hydrogenation of phenylacetylene (0.25 mL)
on Pd-polymer/MS catalysts (0.02 g) in ethanol (25 mL) at 40°C and 0.1 MPa

Catalyst	$W \times 10^{-6}$, mol/s		Selectivity for styrene, %	Conversion, %
	C≡C	C=C		
Pd-PAA(1:5)/MS	0.73	0.82	80.9	96.5
Pd-PAM(1:5)/MS	1.18	1.08	88.0	92.0

The catalyst was easily separated from the reaction medium by magnetic field (Figure 6) at the end of the process indicating the prospect for development of such type of new nanosized magnetic materials for catalysis.



a) b)

Figure 6 – Images of reaction mixture before (a) and after (b) magnetic separation of Pd-PAM/MS catalyst

The next step of study demonstrated the effect of the ratio of active phase components (Pd:PAM = 1:5, 1:10 and 1:15) on the catalytic properties of Pd-PAM/MS. It was found that the reaction rate increased with increasing polymer content in the catalysts. The highest rate (1.36×10^{-6} mol/s) of phenylacetylene hydrogenation showed the catalyst with the ratio of Pd:PAM=1:15 (Figure 7).

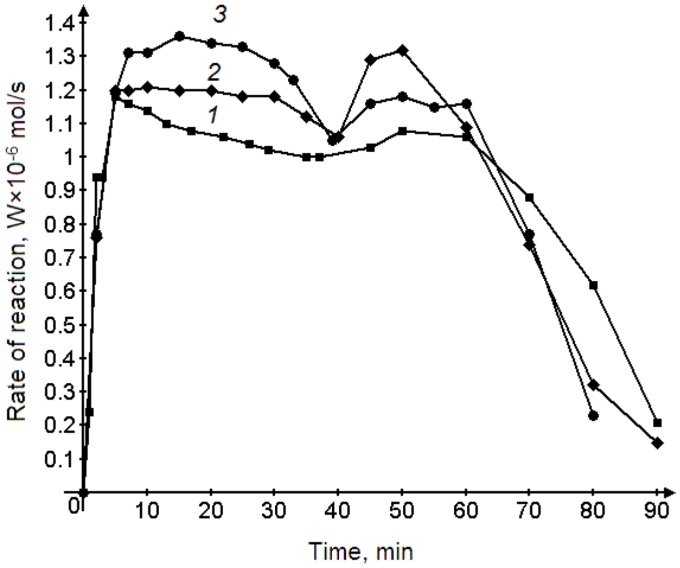


Figure 7 - Changes in the rate of phenylacetylene hydrogenation in the presence of Pd-PAM/MS catalysts: (1) Pd:PAM = 1:5; (2) Pd:PAM = 1:10 and (3) Pd:PAM = 1:15. Conditions: catalyst sample weight, 0.02 g; temperature, 40°C; H_2 pressure, 0.1 MPa; solvent, ethanol (25 mL); and initial phenylacetylene amount, 0.25 mL.

The selectivity for styrene on all studied Pd-PAM/MS catalysts was close to 88-89% at the substrate conversion of 92%. Thus, it has been shown that the activity of the catalysts increases with increasing polyacrylamide polymer content, while the selectivity of the process remains practically unchanged (Table 3). These results can indicate formation of uniform active centers on magnetic support.

Table 3 - Results of the hydrogenation of phenylacetylene (0.25 mL)
on Pd-PAM/MS catalysts (0.02 g) in ethanol (25 mL) at 40°C and 0.1 MPa

Catalyst	$W\times10^{-6}$, mol/s		Selectivity for styrene, %	Conversion, %
	C≡C	C=C		
Pd-PAM(1:5)/MS	1.18	1.08	88.0	92.0
Pd-PAM(1:10)/MS	1.21	1.32	88.1	95.1
Pd-PAM(1:15)/MS	1.36	1.18	89.2	93.0

Conclusion

A simple method for the synthesis of supported palladium hydrogenation catalysts with magnetic properties has been developed. The procedure consisted of mixing a colloidal solution of polymer-stabilized palladium with a suspension of a highly disperse magnetic support (γ-Fe_2O_3). The active phase was fixed due to reducing the surface energy of the magnetic nanoparticles as a result of the adsorption of the polymer-metal complex.

The results of testing the obtained catalysts in the hydrogenation of phenylacetylene have demonstrated their high activity (reaction rates are $0.73\text{-}1.36\times10^{-6}$ mol/s) and selectivity for styrene (80.9-89.2%). The optimum catalytic properties showed the supported palladium composite stabilized with polyacrylamide with Pd:PAA ratio of 1:15. The advantage of the use of magnetic nanosized materials as supports is formation of dispersed catalysts close to colloidal systems and simplicity of their separation from reaction products by magnetic field.

Acknowledgments

The work was carried out with the financial support of the State Committee of Science of the Ministry of Education and Science of the Republic of Kazakhstan (grant AP05130377).

REFERENCES

[1] Lu A-H, Salabas E L, Schuth F (**2007**) Magnetic nanoparticles: synthesis, protection, functionalization, and application, Angew. Chem. Int. Ed., 46:1222-1244. DOI:10.1002/anie.200602866 (in Eng)

[2] Mohammed L, Gomaa H G, Ragab D, Zhu J (**2017**) Magnetic nanoparticles for environmental and biomedical applications: a review, Particuology, 30:1-14. DOI:10.1016/j.partic.2016.06.001 (in Eng)

[3] Wei Y, Han B, Hu X, Lin Y, Wang X, Deng X (**2012**) Synthesis of Fe_3O_4 nanoparticles and their magnetic properties, Procedia Engineering, 27:632-637. DOI:10.1016/j.proeng.2011.12.498 (in Eng)

[4] Khojasteh H, Mirkhani V, Moghadam M, Tangestaninejad S, Mohammadpoor-Baltork I (**2015**) Palladium loaded on magnetic nanoparticles as efficient and recyclable catalyst for the Suzuki-Miyaura reaction, J. Nano Struct., 5:271-280. DOI: 10.7508/jns.2015.03.009 (in Eng)

[5] Liu W, Tian F, Yu J, Bi Y (**2016**) Magnetic mesoporous palladium catalyzed selective hydrogenation of sunflower oil, J. Oleo Sci., 65:451-458. DOI:10.5650/jos.ess15169 (in Eng)

[6] Abu-Reziq R, Wang D, Post M, Alper H (**2007**) Platinum nanoparticles supported on ionic liquid-modified magnetic nanoparticles: selective hydrogenation catalysts, Adv. Synth. Catal., 349:2145-2150. DOI: 10.1002/adsc.200700129 (in Eng)

[7] Guan H, Chao C, Kong W, Hu Z, Zhao Y, Yuan S, Zhang B (**2017**) Magnetic porous PtNi/SiO_2 nanofibers for catalytic hydrogenation of p-nitrophenol, J. Nanopart. Res., 19:187-197. DOI: 10.1007/s11051-017-3884-9 (in Eng)

[8] Zhang J, Wang Y, Ji H, Wei Y, Wu N, Zuo B, Wang Q (**2005**) Magnetic nanocomposite catalysts with high activity and selectivity for selective hydrogenation of ortho-chloronitrobenzene, Journal of Catalysis, 229:114-118. DOI:10.1016/j.jcat.2004.09.029 (in Eng)

[9] Chen H, Zhang P, Tan W, Jiang F, Tang R (**2014**) Palladium supported on amino functionalized magnetic MCM-41 for catalytic hydrogenation of aqueous bromate, RSC Adv., 4:38743-38749. DOI: 10.1039/C4RA05593D (in Eng)

[10] Laska U, Frost C G, Price G J, Plucinski P K (**2009**) Easy-separable magnetic nanoparticle-supported Pd catalysts: kinetics, stability and catalyst re-use, Journal of Catalysis, 268:318-328. DOI:10.1016/j.jcat.2009.10.001 (in Eng)

[11] Zhou P, Li D, Jin S, Chen S, Zhang Z (**2016**) Catalytic transfer hydrogenation of nitrocompounds into amines over magnetic grapheme oxide supported Pd nanoparticles, International Journal of Hydrogen Energy, 41:15218-15224. DOI: 10.1016/j.ijhydene.2016.06.257 (in Eng)

[12] Gyergyek S, Kocjan A, Bjelić A, Grilc M, Likozar B, Makovec D (**2018**) Magnetically separable Ru-based nano-catalyst for the hydrogenation/hydro-deoxygenation of lignin-derived platform chemicals, Mater. Res. Lett., 6:426-431. DOI: 10.1080/21663831.2018.1477847 (in Eng)

[13] Hu A, Yee G T, Lin W (**2005**) Magnetically recoverable chiral catalysts immobilized on magnetite nanoparticles for asymmetric hydrogenation of aromatic ketones, J. Am. Chem. Soc., 127:12486-12487. DOI: 10.1021/ja053881o (in Eng)

[14] Sydnes M O (2017) The use of palladium on magnetic support as catalyst for Suzuki–Miyaura cross-coupling reactions, Catalysts, 7:1-14. DOI:10.3390/catal7010035 (in Eng)

[15] Biglione C, Cappelletti A L, Strumia M C, Martín S E, Uberman P M (**2018**) Magnetic Pd nanocatalyst Fe_3O_4@Pd for C–C bond formation and hydrogenation reactions, J. Nanopart. Res., 20:127-142. DOI: 10.1007/s11051-018-4233-3 (in Eng)

[16] Nasir Baig R B, Varma R S (**2014**) Magnetic carbon-supported palladium nanoparticles: an efficient and sustainable catalyst for hydrogenation reactions, ACS Sustainable Chemistry & Engineering, 2:2155-2158. DOI: 10.1021/sc500341h (in Eng)

[17] Zhou J, Dong Z, Yang H, Shi Z, Zhou X, Li R (**2013**) Pd immobilized on magnetic chitosan as a heterogeneous catalyst for acetalization and hydrogenation reactions, Applied Surface Science, 279:360-366. DOI: 10.1016/j.apsusc.2013.04.113 (in Eng)

[18] Shin J Y, Jung Y, Kim S J, Lee S (**2011**) Supported Pd nanocatalysts onto ionic silica-coated magnetic particles for catalysis in ionic liquids, Bull. Korean Chem. Soc., 32:3105-3108. DOI: 10.5012/bkcs.2011.32.8.3105 (in Eng)

[19] Gawande M B, Rathi A K, Branco P S, Varma R S (**2013**) Sustainable utility of magnetically recyclable nano-catalysts in water: applications in organic synthesis, Appl. Sci., 3:656-674. DOI:10.3390/app3040656 (in Eng)

[20] Mulahmetovic E, Hargaden G C (**2017**) Recent advances in the development of magnetic catalysts for the Suzuki reaction, Review Journal of Chemistry, 7:373-398. DOI: 10.1134/S2079978017030037 (in Eng)

[21] Abu-Dief A M, Abdel-Fatah S M (**2018**) Development and functionalization of magnetic nanoparticles as powerful and green catalysts for organic synthesis, Beni-Suef University Journal of Basic and Applied Sciences, 7:55-67. DOI: 10.1016/j.bjbas.2017.05.008 (in Eng)

[22] Zharmagambetova A K, Seitkalieva K S, Talgatov E T, Auezkhanova A S, Dzhardimalieva G I, Pomogailo A D (**2016**) Polymer-modified supported palladium catalysts for the hydrogenation of acetylene compounds, Kinet. Catal., 57:360-367. DOI: 10.1134/S0023158416030174 (in Eng)

[23] Iconaru S L, Prodan A M, Motelica-Heino M, Sizaret S, Predoi D (**2012**) Synthesis and characterization of polysaccharide-maghemite composite nanoparticles and their antibacterial properties, Nanoscale Research Letters, 7:576. DOI: 10.1186/1556-276X-7-576

[24] Ospanova A K, Ashymhan N S, Berdybek G, Tastanov N (**2014**) Physico-chemical characteristics of complexation processes of transition metal ions with polyelectrolytes [Fiziko-khimicheskiye kharakteristiki protsessov kompleksoobrazovaniya ionov perekhodnykh metallov s polielektrolitami], News of the NAS RK. Series of chemistry and technology [Izvestiya NAN RK. Seriya khimii i tekhnologii], 4:59-65. https://doi.org/10.32014/2018.%202518-1491(In Russian)

ӘОК 541.128.13:542.975’973:541.64

Э.Т. Талғатов, А.С. Әуезханова, Н.Ж. Тумабаев, С.Н. Ахметова,
Қ.С. Сейтқалиева, Е.Ә. Бегмат, Ә.Қ. Жармағамбетова

«Д.В. Сокольский атындағы жанармай, катализ және электрохимия институты» АҚ, Алматы, Қазақстан

ФЕНИЛАЦЕТИЛЕНДІ ГИДРЛЕУГЕ АРНАЛҒАН МАГНИТТІ ТАСЫМАЛДАҒЫШҚА ОТЫРҒЫЗЫЛҒАН ПОЛИМЕР-ПАЛЛАДИЙ КАТАЛИЗАТОРЛАРЫ

Аннотация. Магнитті тасымалдағышқа отырғызылған Pd-полимер катализаторлары адсорбциялық әдіспен дайындалды. Магнитті тасымалдағыш темір хлоридтерін натрий гидроксидімен бірге Fe^{3+}:Fe^{2+} = 2:1 қатынаста біріктіріп отырғызу әдісімен синтезделінді. Палладидің коллоидты ертінділер сериясы полиакриламид (ПАА) және полиакрил қышқылдарының (ПАҚ) қатысуымен әртүрлі палладидың полимерге мольдік қатынасында (Pd:ПАҚ = 1:5; Pd:ПАА = 1:5; Pd:ПАА = 1:10 и Pd:ПАА = 1:15) натрий борогидридімен K_2PdCl_4 тотықсыздандыру арқылы алынды.

Бастапқы компоненттер және катализаторлар физико химиялық әдістермен зерттелінді. РФА нәтижелері синтезделген магнит үлгісі кристалдық беті бойынша шпинальды құрылысы бар маггемитқа сәйкес екендігі көрсетті және бөлшектердің орташа өлшемі 8,5 нм тең. 425 нм кезінде $PdCl_4^{2-}$ иондарының жұтылу сызықтарының жоғалуы палладидың толық қалпына келгенін дәлелдейді. Элементті анализ бойынша катализатордағы палладий мөлшері есептеп алынған нәтижеге жақын және барлық компоненттер суммасының 1мас. % құрайды, яғни магнитті тасымалдағышқа полимермен протектірленген палладий бөлшектерінің отырғанын растайды.

Фенилацетиленді гидрлеуде барлық катализаторлар жоғары белсенділік және стирол бойынша жоғары селективтілік ($W_{C≡C}$ = 0,73-1,36×10^{-6} моль $с^{-1}$, $S_{ст}$ = 80,9-89,2%) көрсетті. ПАА-тұрақтандырылған палладий катализаторы Pd-ПАҚ/МТ катализаторымен салыстырғанда стиролдың шығымы және реакцияның жылдамдығы жоғары болатындығын көрсетті. Полмердің мөлшерін арттыру Pd-ПАА/МТ катализаторының каталитикалық қасиетіне аздап әсер етеді.

Түйін сөздер. Палладий, полимер, магнитті катализатор, гидрлеу, фенилацетилен.

УДК 541.128.13:542.975’973:541.64

Э.Т. Талгатов, А.С. Ауезханова, Н.Ж. Тумабаев, С.Н. Ахметова,
К.С. Сейткалиева, Е.А. Бегмат, А.К. Жармагамбетова

АО «Институт топлива, катализа и электрохимии им. Д.В. Сокольского», Алматы, Казахстан

ПОЛИМЕР-ПАЛЛАДИЕВЫЕ КАТАЛИЗАТОРЫ НА МАГНИТНОМ НОСИТЕЛЕ ДЛЯ ГИДРИРОВАНИЯ ФЕНИЛАЦЕТИЛЕНА

Аннотация. Pd-полимер катализаторы, нанесенные на магнитный носитель (МН), были успешно приготовлены адсорбционным методом. Магнитный носитель синтезировали методом соосаждения хлоридов железа гидроксидом натрия в соотношении Fe^{3+}:Fe^{2+} = 2:1. Серию коллоидных растворов палладия получали путем восстановления K_2PdCl_4 борогидридом натрия в присутствии полиакриламида (ПАА) и полиакриловой кислоты (ПАК) с различным мольным отношением палладия к полимеру (Pd:ПАК = 1:5; Pd:ПАА = 1:5; Pd:ПАА = 1:10 и Pd:ПАА = 1:15).

Исходные компоненты и катализаторы были охарактеризованы физико-химическими методами. Результаты РФА показали, что синтезированный магнитный образец по кристаллическим плоскостям соответствует маггемиту со шпинальной структурой и имеет средний размер частиц 8,5 нм. Исчезновение полосы поглощения ионов $PdCl_4^{2-}$ при 425 нм свидетельствовало о полном восстановлении палладия. Согласно элементному анализу содержание палладия в катализаторах близко к расчетным данным и составляет 1мас.% от суммы всех компонентов, что свидетельствует о количественном закреплении полимер-протектированных частиц палладия на магнитном носителе.

Результаты гидрирования фенилацетилена показали, что все катализаторы проявляют достаточно высокую активность и селективность по стиролу ($W_{C\equiv C}$ = 0,73-1,36×10^{-6} моль $с^{-1}$, $S_{ст}$ = 80,9-89,2%). ПАА-стабилизированный палладиевый катализатор показал более высокую скорость и выход стирола по сравнению с Pd-ПАК/МН катализатором. Увеличение содержания полимера не значительно влияет на каталитические свойства Pd-ПАА/МН катализатора.

Ключевые слова. Палладий, полимер, магнитный катализатор, гидрирование, фенилацетилен.

Information about authors:

Talgatov E.T. - Senior Researcher, Doctor PhD, Laboratory of Organic Catalysis, JSC “D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry”, Almaty, Kazakhstan. Tel: +77272916972, e-mail: eldar-talgatov@mail.ru, ORCID iD 0000-0001-8153-4765;

Auyezkhanova A.S. – Leading Researcher, Candidate of Chemical Sciences, Laboratory of Organic Catalysis, JSC “D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry”, Almaty, Kazakhstan. Tel: +77272916972, e-mail: a.assemgul@mail.ru, ORCID 0000-0002-8999-2864;

Tumabayev N.Z. - Leading Researcher, Candidate of Chemical Sciences, Laboratory of Organic Catalysis, JSC “D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry”, Almaty, Kazakhstan. Tel: +77272916972, e-mail: muhamed_76@mail.ru, ORCID 0000-0002-4871-0541;

Akhmetova S.N. – Junior Researcher, Laboratory of Organic Catalysis, JSC “D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry”, Almaty, Kazakhstan. Tel: +77272916972, e-mail: sn.akhmetova@mail.ru, ORCID 0000-0003-1048-2640;

Seitkalieva K.S. - Junior Researcher, Laboratory of Organic Catalysis, JSC “D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry”, Almaty, Kazakhstan. Tel: +77272916972, e-mail: kuralai_seitkalieva@mail.ru, ORCID 0000-0002-1502-8845;

Begmat Y.A. – Senior laboratory assistant, Laboratory of Organic Catalysis, JSC “D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry”, Almaty, Kazakhstan. Tel: +77272916972, e-mail: begmat1995@mail.ru, ORCID 0000-0002-7308-3471;

Zharmagambetova A.K. - Head of the laboratory of Organic Catalysis, Doctor of Chemical Sciences, Professor, JSC “D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry”, Almaty, Kazakhstan. Tel: +77272916972, e-mail: zhalima@mail.ru, ORCID ID 0000-0002-7494-6005

МАЗМҰНЫ

СОДЕРЖАНИЕ

CONTENTS

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://www.chemistry-technology.kz/index.php/ru/

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

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

Подписано в печать 05.12.2018.
Формат 60x881/8. Бумага офсетная. Печать – ризограф.
9,8 п.л. Тираж 300. Заказ 6.

Национальная академия наук РК
050010, Алматы, ул. Шевченко, 28, т. 272-13-18, 272-13-19