POLYMER-PALLADIUM CATALYSTS ON MAGNETIC SUPPORT FOR HYDROGENATION OF PHENYLACETYLENE

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 (FeCl$_3$ : FeCl$_2$ = 2:1) with sodium hydroxide. A series of colloidal palladium solutions was prepared by reduction of K$_2$PdCl$_4$ 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 spiral structure and an average particle size of 8.5 nm. The disappearance of the absorption band of PdCl$_{2}^{2-}$ ions at 425 nm indicated a complete reduction of palladium. According to elemental analysis, the content of palladium in the catalysts was 1 wt. % 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 ($W_{\text{C}} = 0.73\cdot10^{-6}$ mol/s, $S_{\text{C}} = 80.9-89.2\%$). 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 dispersive 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), PdCl₂ (59-60% Pd, Aldrich), KCl (pure grade), FeCl₃·4H₂O (pure grade), FeCl₃·6H₂O (pure grade), NaBH₄ (96%, Aldrich), NaOH (pure grade), polyacrylamide (PAM, Mₐ = 1000000) and polyacrylic acid (PAA, Mₐ = 1250000, Aldrich) were used without additional purification.

Synthesis of magnetic support (MS)
The iron salts (FeCl₃·6H₂O -21.6 g and FeCl₃·4H₂O - 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 NaBH₄ (10 mL of 0.05 mmol, 1.9 mg) was rapidly added to 90 mL of an aqueous mixture of K₂PdCl₄ (0.1 mmol, 10.6 mg/Pd) 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 spectrophotometrically (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 COMITAx X-ray fluorescence spectrometer.

The prepared colloidal palladium solution (100 mL of 1×10⁻³ 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.
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:NaBH₄ = 2:1. The disappearance of the absorption band of PdCl₂⁺ ions at 425 nm in the spectrum of the reduced sample has confirmed the transition of Pd²⁺ to the zerovalent state (Figure 2).

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.
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 1 wt. % of the sum of all components.

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

<table>
<thead>
<tr>
<th>Element Concentration, wt. %</th>
<th>O</th>
<th>Cl</th>
<th>Fe</th>
<th>Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>29.00</td>
<td>0.77</td>
<td>68.50</td>
<td>1.00</td>
</tr>
</tbody>
</table>

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 \(0.7 \times 10^{-6}\) mol/s which in ~70 minutes insignificantly increased. The sharp slowing of the reaction begins at the 90\(^{th}\) 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.](image)

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).

![Graphs showing reaction mixture composition over time](image)

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; H2 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>
<thead>
<tr>
<th>Catalyst</th>
<th>W×10⁻⁶ mol/s</th>
<th>Selectivity for styrene, %</th>
<th>Conversion, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C=C</td>
<td>C=C</td>
<td></td>
</tr>
<tr>
<td>Pd-PAA(1:5)/MS</td>
<td>0.73</td>
<td>0.82</td>
<td>80.9</td>
</tr>
<tr>
<td>Pd-PAM(1:5)/MS</td>
<td>1.18</td>
<td>1.08</td>
<td>88.0</td>
</tr>
</tbody>
</table>

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

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.

![Images of reaction mixture before and after magnetic separation](image)

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).

![Graph showing changes in the rate of phenylacetylene hydrogenation in the presence of Pd-PAM/MS catalysts.](image)

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; H₂ 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>
<thead>
<tr>
<th>Catalyst</th>
<th>WC=H, mol/s</th>
<th>Selectivity for styrene, %</th>
<th>Conversion, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd-PAM(1:5)MS</td>
<td>1.18</td>
<td>1.08</td>
<td>88.0</td>
</tr>
<tr>
<td>Pd-PAM(1:10)MS</td>
<td>1.21</td>
<td>1.32</td>
<td>88.1</td>
</tr>
<tr>
<td>Pd-PAM(1:15)MS</td>
<td>1.36</td>
<td>1.18</td>
<td>89.2</td>
</tr>
</tbody>
</table>

**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-Fe₂O₃). 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 0.73-1.36×10⁻⁶ 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


Э.Т. Талгатов, А.С. Ауэзханова, Н.Ж. Тумбаев, С.Н. Ахметова, К.С. Сейтекініева, Е.А. Бегмат, А.К. Жармагамбетова

«Д.В. Сокольский атындағы жаңарай, катализ және электролитика институты» АҚ, Алматы, Қазақстан

ФЕНИЛАЦЕТИЛЕНДІ ГИДРЕЛІУЕ АРНАЛҒАН МАГНИТТІ ТАСЫМДАЛАУЫШҚА ОТЫРЫЗЫЛҒАН ПОЛИМЕР-ПАЛЛАДІЙ КАТАЛИЗАТОРЛАРЫ


Бағдарлы компоненттер және катализаторлар физикалық химиялық әдістемен зерттелді. РФА нәтижелері синтезделген магнит ұлғісінің кристалдық бөлік бойынша өміршылық құрылымы бар магнетитка сәйкес сәнді тәрізді қасреті және бөлшектерінің орташа елшемі 8,5 нм тен. 425 нм қосынды PdCl2 өндерінің жұтұрғы сығындығының қоңырлымы палладиұлы әлкілдің өлкілі тұлға размерін қалғанда, арнайы компоненттер сумаының 1мас. % құрылы, яғни магнитті тасымдалғанық полимермен протекцияланған палладий бөлшектерінің отырын жағында.

Фенилациетиллен гидреусті барлық катализаторлар газоры бөлінділік және стирил бойынша газоры селективтілік (W_{G/С} = 0,73-1,38×10^{-5} моль с^{-1}, S_{г} = 80,9-89,2%) көрсететін. ПАА-дұрактанылған палладий катализаторы Pd-ПАА/МТ синтезалыған стирил болып, реакцияның жылдамдығы газоры болыстың көрсетіп. Полимердің молекуляр арттыру Pd-ПАА/МТ катализаторының каталитикалық қасиетіне аздап әсер етеді.

Түйін сөз. Полимер, палладий, магнитті катализатор, гидреу, фенилациетилен.

УДК 541.128.13:542.975’973:541.64

Э.Т. Талгатов, А.С. Ауэзханова, Н.Ж. Тумбаев, С.Н. Ахметова, К.С. Сейтекініева, Е.А. Бегмат, А.К. Жармагамбетова

АО «Институт топлива, катализ и электрохимии им. Д.В. Сокольского», Алматы, Қазақстан

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 K2PdCl4 борогидридом натрия в присутствии полиакриламида (ПАА) и полиакриловой кислоты (ПАК) с различным мольным отношением палладия к полимеру (Pd:ПАА = 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 магнетиту со шпиндельной структурой и имеет средний размер частиц 8,5 нм. Исследование полосы поглощения ионов PdCl$_2$ 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-протеинированных частиц палладия на магнитном носителе.

Результаты гидрирования фенилацетилена показали, что все катализаторы проявляют достаточно высокую активность и селективность по стирилу (W$_{Conv.}$ = 0,73-1,36×10$^{-6}$ моль с$^{-1}$, S$_{sr}$ = 80,9-89,2%). ПАА-стабилизированный палладиевый катализатор показал более высокую скорость и выход стирила по сравнению с Pd-ПАА/МН катализатором. Увеличение содержания полимера не значительно влияет на катализитические 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;
Atayezhanova 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@gmail.ru, ORCID 0000-0002-8471-0541;
Akmetova S.N. – Junior Researcher, Laboratory of Organic Catalysis, JSC “D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry”, Almaty, Kazakhstan. Tel: +77272916972, e-mail: su.akmetova@mail.ru, ORCID 0000-0003-1048-2640;
Setkalieva 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_setkalieva@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;
Zhamargambetova 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: zalina1982@mail.ru, ORCID ID 0000-0002-7494-6005