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ИЗВЕСТИЯ

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

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

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

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zhalima@mail.ru**POLYSACCHARIDE-STABILIZED PALLADIUM NANOCATALYST
FOR SEMI-HYDROGENATION OF COMPLEX ALKYNOLS**

Abstract. New Pd-Polysaccharide/ZnO catalysts with palladium content of 0.1%, 0.3%, 0.5% and 1.0% have been developed and tested in the hydrogenation of long-chain acetylenic alcohols used as precursors for syntheses of vitamins and pest-insect pheromones. Pectin and gellan were used as stabilizers of Pd nanoparticles (1-2 nm) fixed on ZnO. TEM study confirmed uniform distribution of the dispersed metal on the surface of zinc oxide. The sizes of palladium nanoparticles in the best catalyst were 1-2 nm. The catalysts with 0.5%wt.Pd demonstrated the highest activity, selectivity to cis-alkenols and stability in multiple runs. TON is varied in the range of 6700-7500 for hexadecynols. TON was 33000 for hydrogenation of 3,7,11,15-tetramethylhexadecyn-1-ol-3 (C₂₀). A total hydrogenated amount of this substrate on .05 g of 0.5% Pd-Pec/ZnO catalyst was 48 ml. Deactivation of the catalysts is observed after 64 runs. TEM images showed partial leaching of twisted polymer-metal films from the surface of ZnO.

Keywords. Pectin, gellan, polysaccharides, catalytic properties, hydrogenation, palladium catalysts, alkynols.

Introduction

The principles of green chemistry [1] are targeting to develop energy-saving selective processes for the production of valuable chemicals. Many monomers and plasticizers, aromatic substances, vitamins, pheromones, medicines and other biologically active substances are synthesized catalytically based on a selective hydrogenation of long-chain (C₁₀-C₂₀) acetylene compounds into olefin derivatives [2-9]. These reactions are often carried out at high temperatures and pressures with rather low yields of targeted products. In this case the selection of the proper catalyst is very important. The use of modern nanotechnology approaches for creating new types of nanosized catalysts makes it possible to improve these drawbacks.

Supported catalysts are usually used in the chemical industry, energy, and environmental protection. This is due to the fact that their properties depend on the structure and sizes of the active phase. Reducing its content in the surface of the support leads to a decrease in the particle sizes of the deposited metals and an increase in the number of active centers for catalytic acts and therefore to an increase in the rate and selectivity of the reaction. Polymers with different functional groups are used as one of the nanotechnology approach to synthesize metal nanoparticles and catalysts [10-15]

We have developed a simple method of catalyst preparation based on interaction and stabilization of metal nanoparticles by polymers on the surface of inorganic sorbents (natural and synthetic zeolites, metal oxides) [16, 17]. The developed technique allows to obtain catalysts for selective hydrogenation of wide range of unsaturated compounds [16-22].

The present work demonstrates the possibilities of using an environmentally friendly natural polymers as pectin and gellan to stabilize palladium nanoparticles on the surface of zinc oxide. The developed low-percentage catalysts were studied in the semi-hydrogenation of complex acetylene alcohols. The obtained olefin derivatives are used in the syntheses of vitamins and pest insect pheromones [5].

Experimental part

The method of sequential adsorption of polymer and metal salt from water solutions was used for the preparation of palladium catalysts [22].

The acetylenic alcohols: 3,7,11,15-tetramethylhexadecan-1-ol-3 (C₂₀); 9-hexadecan-1-ol (9-HD-1-ol) and 11-hexadecan-1-ol (11-HD-1-ol) were purchased from Sigma Aldrich and used without additional purification.

Ethanol (reagent grade), palladium chloride (PdCl₂, 59-60% Pd, Sigma Aldrich), pectin (Pec, M_w = 15000, the content of uronide components is 90.3%, the degree of esterification is 23.7%, Sigma Aldrich) were also used without additional purification. Zinc oxide (chemically pure) was used as an inorganic support.

Palladium amount in the Pd-Pec/ZnO catalysts was varied from 0.1 to 1.0 wt.% from total composite content. The palladium content in mother liquors before and after metal adsorption was determined from photoelectric colorimetry data, which were obtained on a SF-2000 UV/Vis spectrophotometer (OKB Spectr, Russia) based on calibration curves constructed at the wavelength $\lambda = 425$ nm.

TEM (transmission electron microscopy) of catalyst samples were studied on a JEM-2100 transmission electron microscope (Jeol, Japan) with an accelerating voltage of 100 kV.

The acetylenic alcohol hydrogenation was carried out in thermostatic reactor in ethanol (25 ml) at 40°C and atmospheric hydrogen pressure. Before the reaction the catalyst was saturated with hydrogen for 30 minutes and the tested substrate was injected to the reactor. Hydrogen uptake was measured and reaction products were detected by chromatographic analysis ("Khromos", Russia). The catalyst selectivity was calculated as the proportion of the target product to the sum of all reaction products at a given conversion.

Results and Discussion

The developed Pd-Pec/ZnO catalysts with 0.1wt.%; 0.3wt.%; 0.5wt.% and 1.0wt.% of Pd have been tested in the hydrogenation of 3,7,11,15-tetramethylhexadecan-1-ol-3 (C₂₀); 9-hexadecan-1-ol (9-HD-1-ol) and 11-hexadecan-1-ol (11-HD-1-ol). The produced olefins of the semi-hydrogenation of these complex acetylene compounds are used in fine chemistry for production of biologically active substances.

The C₂₀ acetylene alcohol is hydrogenated with high rate and stability at multiple runs on the same 1% Pd-Pec/ZnO catalyst sample (Table 1). However, the selectivity to the olefin alcohol is quite low (49.9%). Probably, the alkenol is reduced to 3,7,11,15-tetramethylhexadecanol-3 without desorption from the catalyst into the reaction medium.

Table 1 - Hydrogenation of C₂₀ acetylene alcohol on Pd-Pec/ZnO catalysts with various content of palladium

Pd content, %	W*10 ⁻⁴ , mol/l c	S, %	TON
Pd-Pec/ZnO			
1,0	14.8	49.9	10000
0,5	6.6	89.4	33000
0,3	1.7	58.3	550
0,1	0.8	66.1	-
Reaction conditions: 0.05g catalyst; C ₂₀ = 0.75 ml; 25 ml ethanol; T-40°C; P-1 atm			

A decrease in the metal content in the catalysts from 1.0 to 0.1% leads to a significant decrease in the reaction rate, but the selectivity of the process passes through a maximum attributable to the catalyst with 0.5% metal content (Table 1). It was shown that in 4 minutes the total acetylene alcohol was converted to the olefinic alcohol on this catalyst (Figure 1).

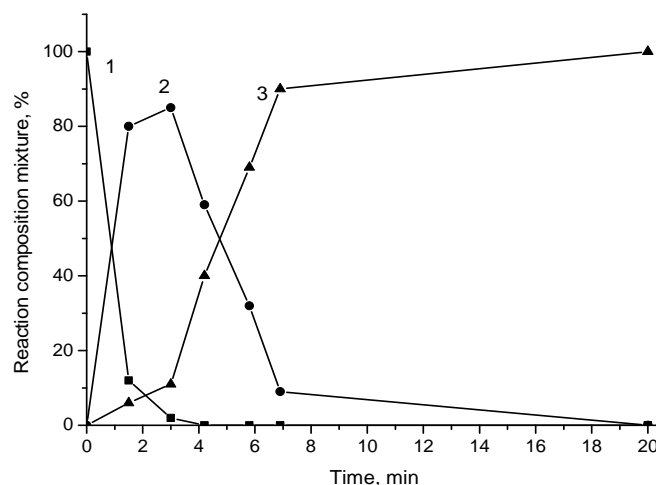


Figure 1 - Hydrogenation of C₂₀ acetylene alcohol on 0.5% Pd-Pec/ ZnO. Diagram of the composition of the reaction mixture: (1) C₂₀ acetylnic alcohol, (2) C₂₀ olefinic alcohol, (3) C₂₀ alcanol. Reaction conditions: catalyst sample weight, 0.05 g; temperature, 40°C; H₂ pressure, 0.1 MPa; solvent, ethanol (25 mL); initial C₂₀ acetylene alcohol amount, 0.25 mL

The amount of the saturated alcohol at this time does not exceed 8%. This catalyst also showed the highest stability. TON reaches 33,000 (catalytic acts per 1 palladium atom).

The catalyst was washed with water after 39, 57 and 64 runs of C₂₀ alcohol hydrogenation [21]. This treatment lead to a noticeable increase in the reaction rate. A total amount of substrate hydrogenated on .05 g of 0.5% Pd-Pec/ZnO catalyst was 48 ml.

According to the TEM data, the initial catalyst (Figure 2, a) is characterized by the uniformly distributed palladium nanoparticles (1-2 nm) in a bulk polymer matrix fixed on the support. A change in the texture of the surface polymer-metal composite is observed in the catalysts' samples taken after 39, 57 and 64 hydrogenation runs. The polymer matrix swelled in the sample tested after the 64 run (Figure 2, c), a partial peeling of the surface polymer layer is observed on the catalyst. New structures have also been observed. (Figure 2, d). Twisted polymer-metal films in a form of "stars" were appeared separately from support.

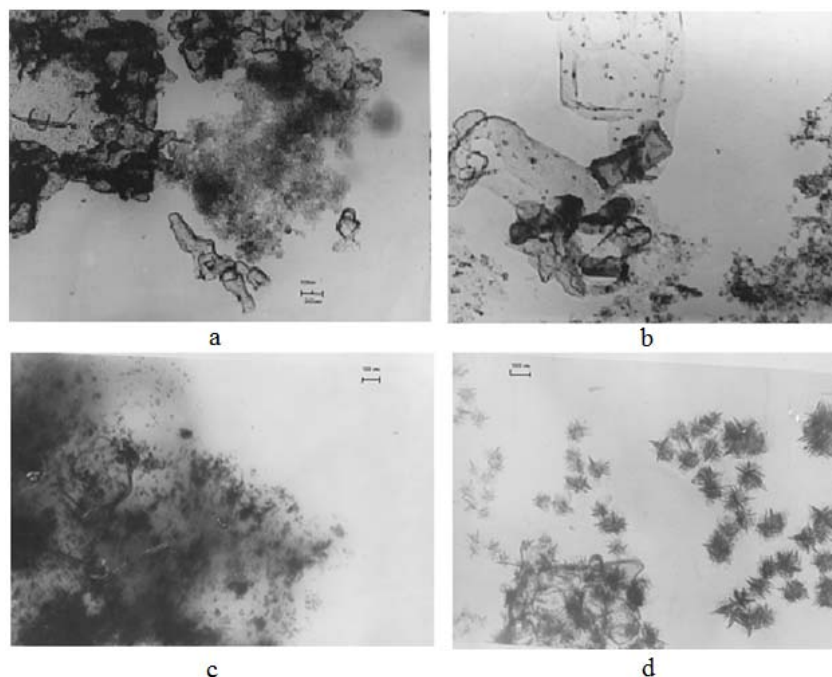


Figure 2 – Microphotographs (TEM) of Pd-Pec/ZnO catalyst. a - initial; b - after 39 runs; c and d - after 64 runs

The introducing gellan instead of Pec leads to the formation of a less active, but more selective catalyst. Such behavior can be explained by differences in the structure of these polysaccharides. Pectin is characterized by one sucrose group in the monomer, as well as a gellan has four such groups. The process slows down sharply after the nearly complete conversion of C₂₀ alkynol to alkenol on 0.5%Pd-Gel/ZnO catalyst. Selectivity reaches 96% (Figure 3).

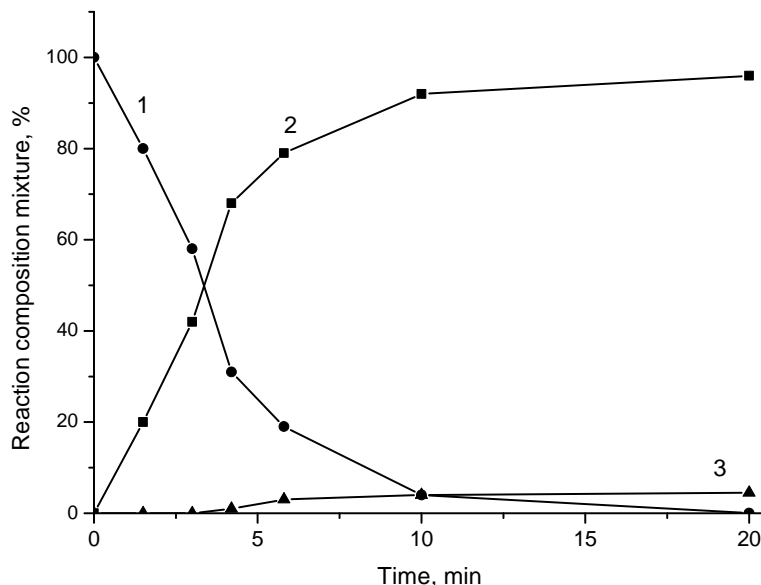


Figure 3 - Hydrogenation of C₂₀ acetylene alcohol on 0.5% Pd-Gel/ZnO. Diagram of the composition of the reaction mixture: (1) C₂₀ acynol; (2) C₂₀ alkenol; (3) C₂₀ alkanol. Reaction conditions: m_{кат}-0,05g; ethanol-25ml; T-40⁰C; P-1 atm

Thus, polysaccharide containing catalysts are complex composites including bulk polymer layer with dispersed palladium nanoparticles inside, which is chemisorbed on the surface of ZnO. The catalysts showed high activity and selectivity in semi-hydrogenation of acetylenic alcohols. It is confirmed by hydrogenation of hexadecynols.

Hydrogenation of 9-hexadecyn-1-ol (9-HD1-ol) and 11-hexadecyn-1-ol (11-HD-1-ol) into cis-alkenols is the most important reaction in synthesis of some pect insect pheromones [6]. The results of the hydrogenation are presented in the Table 2.

It was found that the hydrogenation of 9-HD-1-ol on 0.3 and 0.5% catalysts proceeds at almost the same rates ($2.4-2.9 \cdot 10^{-4}$ mol/l s). In the case of 9-HD-1-ol, the activity of the catalyst increases with increasing palladium content. At the same time, the selectivity of the process on all studied catalysts reaches 100%.

Table 2 – The results of hydrogenation of hexadecyns on Pd-Pec/ZnO and Pd-Gel/ZnO catalysts

Pd content in catalysts, wt. %	W*10 ⁻⁴ , mol/l s	S _{cis-C=C} , %	TON
Pd-Pec/ZnO			
11-hexadecyn-1-ol			
0.1	1.9	100	-
0.3	2.4	100	4400
0.5	2.9	100	7200
9-hexadecyn-1-ol			
0.1	4.7	100	-
0.3	12.2	100	-
0.5	26.2	100	6700
Pd-Gel/ZnO			
11-hexadecyn-1-ol			
0.5	2.7	100	7500
9-hexadecyn-1-ol			
0.5	3.3	100	6900
Reaction conditions: 0.05g catalyst; 25 ml ethanol; T-40 ⁰ C; P-1 atm			

According to chromatographic analysis, in the first 5 minutes, around all of the starting acetylene alcohol is converted to cis-olefin on 0.5% Pd-Pec/ZnO (Figure 4). Only trace amounts of saturated alcohol are detected in the reaction mixture. This catalyst also demonstrates maximum stability during repeated process runs, TON = 6700-7200 (Table 2).

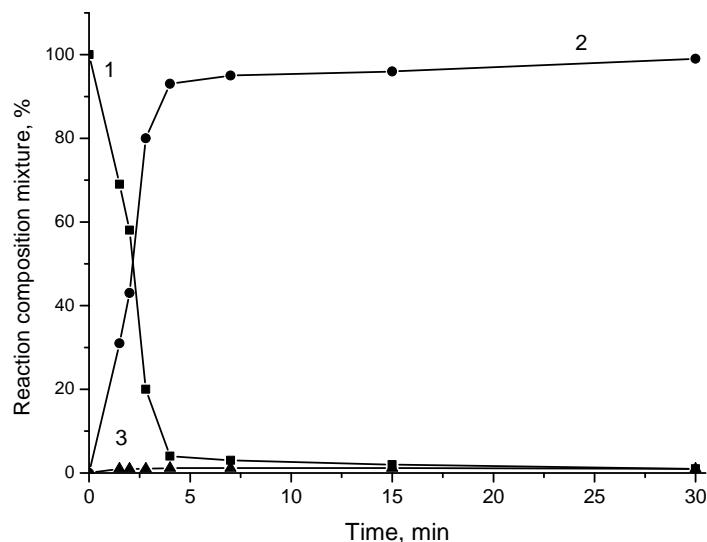


Figure 4 - Hydrogenation of 9-HD-1-ol on 0.5% Pd-Pec/ ZnO. Diagram of the composition of the reaction mixture: (1) C alkynol; (2) C alkenol; (3) C₀ alkanol. Reaction conditions: $m_{\text{кат}}$ -0,05g; ethanol-25ml; T-40°C; P-1 atm

In contrast to the catalyst modified with Pec, the hydrogenation rate of both of 9-hexadecan-1-ol and 11-hexadecan-1-ol on 0.5% Pd-Gel/ZnO is lower (Table 2) while selectivity to cis-alkenol remains 100% and TON also rather high.

Thus, the developed 0.3-0.5% Pd-Pec/ZnO and 0.5% Pd-Gel/ ZnO catalysts are active, stable and stereoselective hydrogenation catalysts for hydrogenation of complex acetylene alcohols.

Conclusions

Thus, taking into account the principles of green chemistry, the low-percentage palladium catalysts stabilized with polysaccharides have been developed. The process of their synthesis was carried out at ambient conditions from water solutions. These catalysts are characterized with high dispersion of Pd nanoparticles (1-2 nm) evenly distributed on the surface of zinc oxide. The catalyst with 0.5% of Pd demonstrated high activity, stability and selectivity in semi-hydrogenation of complex alkynols. The obtained alkenols are used as biologically active substances, as vitamins and insect pheromones used in agriculture to predict the development of insect pests and reduce the number of field treatments with toxic pesticides.

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АЛКИНОЛ КОМПЛЕКСТЕРІН ЖАРТЫЛАЙ ГИДРЛЕУГЕ АРНАЛҒАН ПОЛИСАХАРИД-ТҮРАҚТАЛҒАН ПАЛЛАДИЙ НАНОКАТАЛИЗАТОРЛАРЫ

Аннотация. Құрамында 0,1%, 0,3%, 0,5% және 1,0% Pd болатын жаңа Pd-полисахарид/ZnO катализаторлары витаминдер мен пектинді жәндіктердің феромондарын синтездеу үшін прекурсорлар ретінде қолданылатын ұзын тізбекті ацетилен спирттерін гидрлеу үрдісі үшін әзірленді. Пектин мен гелан ZnO

бекітілген, Pd (1-2 нм) нанобөлшектерін тұрақтандырғыш ретінде пайдаланылды. ТЕМ зерттеуі дисперсті металдың мырыш оксидінің бетіне біркелкі таралуын растады. Ең жақсы катализатордағы палладий нанобөлшектерінің мөлшері 1-2 нм болды. Құрамында Pd мөлшері 0,5% болатын катализаторлар ең жоғары белсенділікті, цис-алкенолдар үшін селективтілікті және қайталама сынақтарда тұрақтылықты көрсетті. ТОН гексадеколиндер үшін 6700-7500 аралығында болады. ТОН 3,7,11,15-тетраметилгексадекин-1-ол-3 (C₂₀) гидрлеу үрдісі үшін 33000 құрайды. 0,5% Pd-ПЕК/ZnO катализаторының 0,05 г дейін гидрленген субстраттың жалпы мөлшері 48 мл болды. Катализатордың дезактивациясы 64 өтпеден кейін байқалады. ПЭМ көмегімен алынған суреттер ZnO бетінен бұралған полимерлі-металл пленкалардың жартылай сілтісіздігін көрсетті.

Түйін сөздер. Пектин, геллан, полисахаридтер, каталитикалық белсенділік, гидрлеу, палладий катализаторы, алкинолдар.

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ПОЛИСАХАРИД-СТАБИЛИЗОВАННЫЕ НАНОКАТАЛИЗАТОРЫ ПАЛЛАДИЯ ДЛЯ ПОЛУГИДРИРОВАНИЯ КОМПЛЕКСОВ АЛКИНОЛОВ

Аннотация. Новые Pd-полисахарид/ZnO катализаторы с содержанием палладия 0,1%, 0,3%, 0,5% и 1,0% были разработаны и испытаны в гидрировании длинноцепочечных ацетиленовых спиртов, используемых в качестве прекурсоров для синтеза витаминов и феромонов насекомых. Пектин и геллан использовали в качестве стабилизаторов наночастиц Pd (1-2 нм), закрепленных на ZnO. ТЕМ исследование подтвердило равномерное распределение дисперсного металла на поверхности оксида цинка. Размеры наночастиц палладия на лучшем катализаторе составляли 1-2 нм. Катализаторы с содержанием 0,5% Pd продемонстрировали наивысшую активность, селективность по цис-алкенолам и стабильность при многократном использовании. ТОН варьируется в диапазоне 6700-7500 для гексадецинолов. ТОН при гидрировании 3,7,11,15-тетраметилгексадецин-1-ол-3 (C₂₀) составляет 33000. Общее количество прогидрированного субстрата на 0,5% Pd-ПЕК/ZnO катализаторе с массой 0,05 г составило 48 мл. Дезактивация катализаторов наблюдается после 64 порции. Данные ПЭМ показали частичное выщелачивание скрученных полимер-металлических пленок с поверхности ZnO.

Ключевые слова. Пектин, геллан, полисахариды, каталитическая активность, гидрирование, палладиевые катализаторы, алкинолы.

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