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ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
АО «Институт топлива, катализа и
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NEWS

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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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SYNTHESIS AND CATALYTIC PROPERTIES OF COMPOSITES WITH Pd-(2-HYDROXYETHYL CELLULOSE) ON BENTONITE

Abstract. Palladium composites based on 2-hydroxyethylcellulose (HEC) and bentonite (BT) have been synthesized to use them as “green” catalysts for the process of phenylacetylene hydrogenation under mild conditions. The introduced amount of HEC in the composites was 5, 10, and 20%. Viscometer method shows the degree of polymer fixation on the surface of the mineral sorbent. The HEC/BT systems with polymer content of 4.1; 9.0; 18.9% have been obtained. Samples of the obtained HEC-containing composites were characterized by X-ray, scanning and transmission electron microscopy. The data obtained have confirmed the fixing of the polymer on the surface of support.

The sorption capacity of the developed HEC-bentonite composites to Pd²⁺ ions has been studied. The content of palladium in the prepared composites decreased with the increasing of HEC amount in the [Pd(HEC)BT] systems and were : 0.9% Pd-BT/HEC (4%), 0.8% Pd-BT / HEC (9%), 0.6% Pd-BT / HEC (19%). To compare the activity and selectivity of composites with different content of HEC in phenylacetylene hydrogenation, the catalysts with the equal palladium content (0.6%) have were prepared. The developed catalysts showed high activity in the hydrogenation at 40°C and atmospheric pressure of hydrogen. The most effective was 0.6% Pd-BT/HEC composite with a HEC content of 9%, the selectivity to styrene was 92.0% with 96.4% conversion of the phenylacetylene.

Keywords. 2-Hydroxyethylcellulose, polysaccharides, bentonite, catalytic activity, hydrogenation, palladium catalysts.

Introduction

Recently, the design of catalytic systems with the natural plant components is in the focus of scientific interests [1-19] as renewable and environmentally friendly raw materials for chemical syntheses [20]. Polysaccharides, such as cellulose, chitosan, pectin, containing of various functional groups in their structures are able to form complexes with metal ions [21, 22]. Cellulose is one of the most promising polysaccharides for developing catalytic systems [15-17] due to its hydrophilicity, chirality, biodegradability, wide chemical modifying ability, and a large surface area. The disadvantage of cellulose in the synthesis of complex compounds with metal ions is its insolubility in water. Therefore, in this work, hydroxyethylcellulose (HEC), was used as a soluble cellulose modification for catalyst preparation.

Catalytic properties of the developed palladium catalysts supported on HEC-modified bentonite have been tested in hydrogenation of phenylacetylene under mild conditions.

Experimental part

The method of sequential adsorption of polymer and metal salt from water solutions was used for the preparation of palladium catalysts [23].

A natural sorbent - bentonite (BT) was used as a support. A cellulose derivative, 2-hydroxyethylcellulose, was chosen as the nanoparticle stabilizer. The polymer amount was chosen to

obtain composites of support with 5%, 10% and 20wt.% of the polysaccharide. Palladium chloride was used to prepare the catalysts with 1 wt. % of Pd. The metal ion concentration in the catalyst after adsorption was determined on an SF-2000 spectrophotometer (Russia, 2015) using calibration curves. Calibration was based on the measure of concentration of series of standard palladium solutions.

IR spectra were obtained on Karl Zeiss Specord-IR-75 spectrometer in the range of 4000-400 cm^{-1} .

The morphology and structure of the initial bentonite and bentonite-based HEC-containing composites as well as sizes of metal nanoparticles were examined by scanning and transition electron microscopy.

The phenylacetylene hydrogenation reaction 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

Synthesis of polysaccharide-silicate composites (PSC) was carried out at room temperature and included the following stages:

- adding of a polymer solution to an aqueous suspension of bentonite;
- stirring the PSC for 2 hours;
- precipitation of the polymer in suspension of the support for 24 hours;
- washing and drying the PSC at room temperature.

The scheme of catalysts' preparation is presented on the Figure 1.

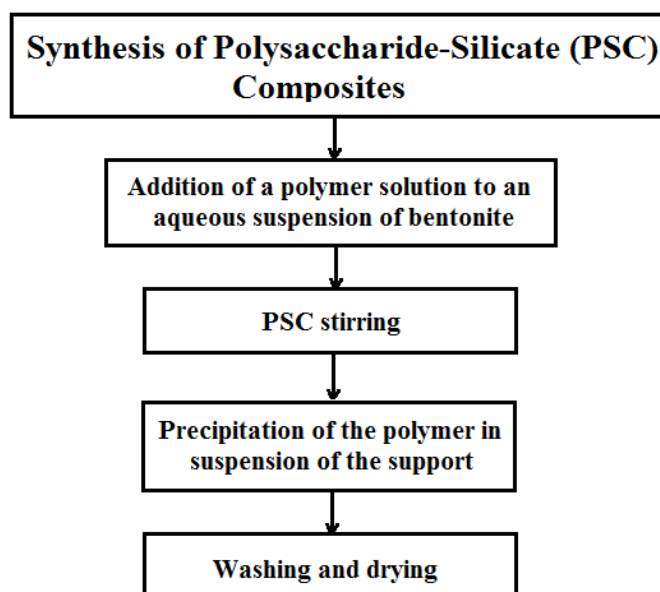


Figure 1 – The scheme for production of polysaccharide-inorganic composites

The concentration of the polymer in the mother liquor of composite was determined using a viscosity calibration curve. The amount of adsorbed polymer was determined by the difference in mass of polymer in the mother liquor before and after sorption. Calculated results of actual content of the polymer in composites are presented in Table 1. It has been shown that the degree of HEC adsorption increases from 81.7 to 94.6% with an increase in the amount of polymer introduced.

Table 1 - Adsorption of HEC on BT

The amount of entered HEC, %	% precipitated HEC from the entered initial amount	The content of HEC in the HEC/BT, %
5.0	81.7	4.1
10.0	90.2	9.0
20.0	94.6	18.9

The presence of polysaccharides in the composites also demonstrated by IR spectroscopic data, according to which the absorption bands of asymmetric and symmetric stretching vibrations of -CH groups of HEC in the range of 2950-2800 cm^{-1} were appeared in the spectra of composites (Table 2). In addition, a shift in the absorption bands of the deformation vibrations of polysaccharide -OH groups in the range of 1450– 1350 cm^{-1} was observed. These changes can be explained by the formation of hydrogen bonds between the oxygen-containing groups of the polymer and OH-centers of bentonite confirming chemisorption of HEC on the surface of the aluminosilicate.

Table 2 – IR spectroscopy data of the studied samples

Sample	νOH	νCH	δOH $\delta\text{C-OH}$	$\delta\text{OH(BT)}$ $\nu\text{Al-O}$
BT	3620 3457	-	-	1141 820 525
HEC	3424	2919 2973	1415 1386	
HEC/BT	3620 3416	2925 2876	1422 1381	1042 796 519
Pd-HEC/BT	3619 3432	2938 2872	1462	1046 801 522

The slight shift in bands characteristic to -OH and Al-O groups indicates the participation of BT hydroxy groups in the binding of polymer (Table 2).

According to scanning microscopy testing, an enlargement and aggregating of HEC-bentonite species (Figure 2, a) to compared with initial bentonite (Figure 2, b) were observed due apparently to the coating of the aluminosilicate with the polysaccharide.

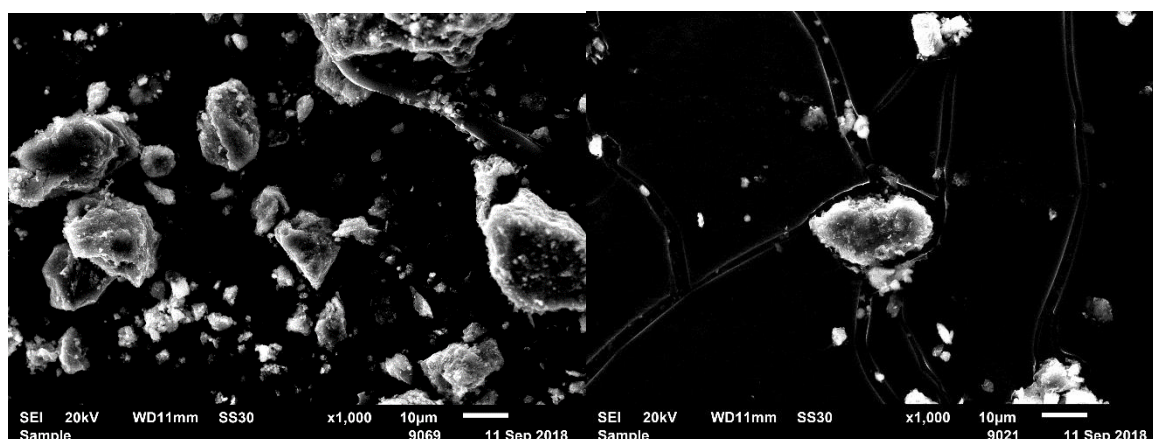


Figure 2 – SEM images of HEC(9%)/BT (a) and Bentonite (b)

In order to obtain catalysts, the solution of palladium (II) salt was dropwise added into the suspension of HEC-bentonite composite in the amount corresponding to the formation of 1%Pd-HEC/bentonite system. Figure 3 provides a general scheme for the preparation of the supported polymer-modified catalysts.

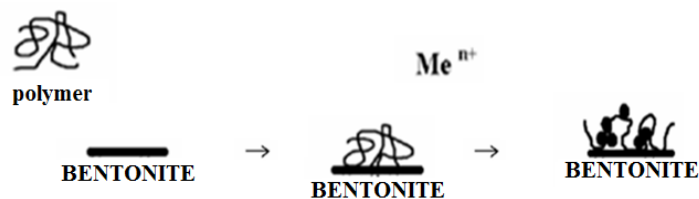


Figure 3 – Scheme of the formation of HEC-based catalysts

The content of metal immobilized on the polymer-modified surface of inorganic material was determined from the change in the concentration of metal ions in the mother liquor before and after sorption. Data on sorption are presented in the Table 4.

It is shown that the degree of deposition of palladium ions on the HEC modified bentonite decreases with an increase in the content of polysaccharide on the composites (Table 4).

Table 4 - Sorption of Palladium Ions on HEC/BT Composites

Composite	$m_{Me} \cdot 10^{-3}$ in the initial solution, g	$m_{Me} \cdot 10^{-3}$ in solution after sorption, g	The degree of adsorption		The metal content in catalyst, %
			$m_{Me} \cdot 10^{-3}$, g	%	
4% HEC/BT	1.91	0.28	1.63	85.30	0.85
9% HEC/BT	1.91	0.30	1.61	84.30	0.84
19% HEC/BT	1.91	0.86	1.05	55.00	0.55

The IR spectroscopy data (Table 2) showed the shifts of the absorption bands of the HEC functional -OH and -C-OH groups in the in the region of $1450-1350 \text{ cm}^{-1}$ of the in spectrum of three-component Pd-HEC/BT composites. The shift in the absorption bands of the -CH-group valence vibration indicates change in the conformation of the polysaccharide and interaction of palladium ions with the polymer layers of HEC/BT.

According to TEM images, the obtained Pd-HEC/BT composites are characterized by agglomerates consisting of nanosized (4-10 nm) palladium particles (Figure 4).

Thus, palladium containing composites based on natural materials like modified cellulose and bentonite have been prepared. Interaction of the components was confirmed by IR-spectroscopy and electrom microscopy. The polysaccharide contributes to the formation of uniform palladium nanoparticles, which form clusters on the surface of bentonite coated with a polymer. The amount of Pd in the composites depends on the quantity of the HEC in the composite. The smallest amount of Pd (0.6wt.%) was detected on the HEC/BT with the content of the polymer of 19%.

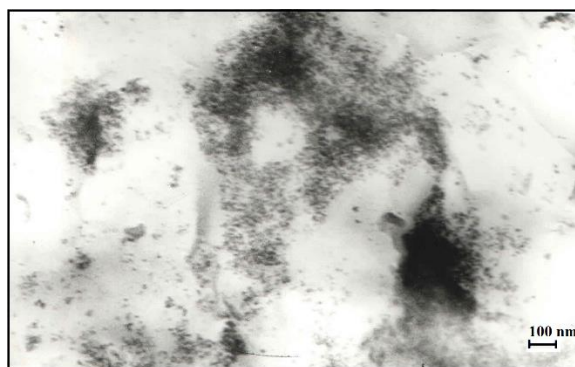
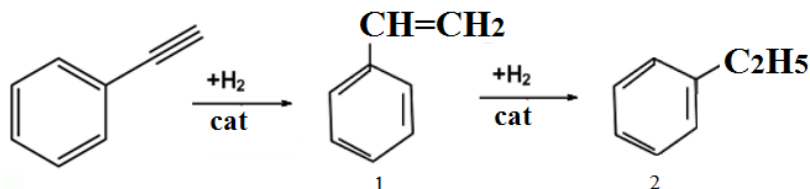


Figure 4 – TEM images of Pd-HEC/BT

To compare catalytic properties of the composites with different HEC content, the catalysts with 0.6 wt.% of palladium was prepared.

The liquid phase hydrogenation of phenylacetylene was chosen as a model reaction.

Phenylacetylene is hydrogenated with formation of styrene (1) which then reduced to ethylbenzene (2):



The hydrogenation rate is increased with the increasing of polymer content in the catalysts from 4% to 9% (Table 5). The further increase of the polysaccharide percentage in the catalyst lead to a decrease in its effectiveness. The optimal palladium catalyst contained 9% HEC and was characterized with the selectivity to styrene of 92% at 96.4% conversion of the substrate (Table 5).

It can be assumed that the reason of low hydrogenation selectivity on the catalyst with a low HEC content (4%) was incomplete coating of the surface of bentonite with a polymer, and part of the palladium was adsorbed directly on the bentonite, and as a result the catalytic centers can be heterogeneous. In the case of an excess amount of polymer in the catalyst (19%), the reason for the low selectivity may be the difficulty of transporting the substrate to the active palladium centers located inside the macromolecular network.

To prove this assumption, it is necessary to conduct additional studies of synthesized catalysts. At the same time, the obtained results confirm the possibility and prospectiveness of using natural materials, such as cellulose and bentonite, to produce complex three-component polymer-inorganic composites with fixed transition metal nanoparticles and to use them as catalysts.

Table 5 – Results of the Hydrogenation of Phenylacetylene on 0.6% Pd/BT-HEC catalysts with different polymer content

Catalyst	Reaction rate, W*10 ⁻⁶ , mol/s		Selectivity to styrene, %	Conversion, %
	C≡C	C=C		
Pd/BT-HEC (4%)	3.2	2.7	82.2	70.3
Pd/BT-HEC (9%)	3.2	3.7	92.1	96.4
Pd/BT-HEC (19%)	3.1	3.1	87.2	90.5

Note – Experimental conditions: T=40°C; P=1 atm; m_{cat}=0.05g; solvent – ethanol.

Conclusions

A HEC-based polysaccharide-silicate composite with varying amounts of polymer (5%, 10%, and 19%) has been obtained by the adsorption method. The preparation method of composites eliminates high-temperature calcination and recovery. By the viscometer method, it was found that the degree of adsorption of HEC varies within 81.7-94.6%. The presence of polysaccharides in the composition of the obtained composites was confirmed by IR spectroscopy, TEM and SEM. It was established that a change in the amount of polymer in the composition of the catalyst affects the selectivity of the hydrogenation process. The prospects of using polysaccharide-silicate composites as components of hydrogenation and oxidation catalysts are shown. Such systems can be attributed to a new generation of "green" catalysts.

The optimal catalyst for the hydrogenation of phenylacetylene is a palladium HEC/BT catalyst with a HEC content of 9%, the selectivity of which for styrene was 92% at 96.4% conversion of the substrate.

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БЕНТОНИТТИҢ БЕТІНДЕ Pd-2-ГИДРОКСИЭТИЛЦЕЛЛЮЛОЗА БАР КОМПОЗИТТЕРДІҢ СИНТЕЗІ МЕН КАТАЛИТИКАЛЫҚ ҚАСИЕТТЕРІ

Аннотация. Жұмсақ жағдайда фенилацетиленді гидрлеу процесінде «жасыл» катализатор ретінде пайдалану үшін 2-гидроксиэтилді целлюлоза (ГЭЦ) және бентонит (БТ) негізінде палладий ГЭЦ-силикатты композиттер синтезделді.

Композиттер құрамындағы ГЭЦ-ның есептік саны 5, 10 және 20% құрады. Вискозиметриялық әдіспен минералды сорбенттің бетіне полимердің бекітілу дәрежесі көрсетілді.

Құрамында 4,1, 9,0, 18,9% полимері бар ГЭЦ/БТ жүйелері алынды. Алынған ГЭЦ-құрамды композиттер ИКС, сканерлейтін және жарық түсіретін электрондық микроскопия әдістерімен сипатталған. Алынған мәліметтер тасымалдаушының бетіне полимердің бекітілгенін растады.

Pd²⁺ иондарына қатысты әзірленген ГЭЦ-силикатты композиттердің сорбциялық белсенділігін зерттеу бойынша жұмыстар жүргізілді. Әзірленген композиттердің құрамында палладийдің құрамы ГЭЦ мөлшерінің ұлғаюымен азайды: 0,9% Pd-П/ ГЭС (4%), 0,8% Pd-БТ/ГЭЦ (9%), 0,6% Pd-БТ/ГЭЦ (19%). Құрамында ГЭЦ бар композиттердің белсенділігі мен селективтілігін салыстыру үшін палладий мөлшері бірдей (0,6%) катализаторлар дайындалды.

Әзірленген палладий катализаторлары 40°C температурада және сутегінің атмосфералық қысымында фенилацетиленді гидрлеу реакциясында белсенділік көрсетті. Ең жоғары тиімділікке құрамында 9% ГЭЦ бар 0,6% Pd-БТ/ГЭЦ композит ие, оның қатысында субстраттың конверсиясы кезінде 92,0% болған стирол бойынша талғампаздылық 96,4% құрады.

Түйін сөздер: 2-гидроксиэтилді целлюлоза, полисахаридтер, бентонит, каталитикалық белсенділік, гидрлеу, палладий катализаторлары.

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СИНТЕЗ И КАТАЛИТИЧЕСКИЕ СВОЙСТВА КОМПОЗИТОВ С Pd-2- ГИДРОКСИЭТИЛЦЕЛЛЮЛОЗОЙ НА БЕНТОНИТЕ

Аннотация. Синтезированы палладиевые ГЭЦ-силикатные композиты на основе 2-гидроксиэтилцеллюлозы (ГЭЦ) и бентонита (БТ) с целью применения их в качестве «зеленых» катализаторов для процесса гидрирования фенилацетилена в мягких условиях. Расчетное количество ГЭЦ в составе композитов составляло 5, 10 и 20%. Вискозиметрическим методом показана степень закрепления полимера на поверхности минерального сорбента. Были получены ГЭЦ/ БТ системы с содержанием полимера 4,1, 9,0, 18,9%. Образцы полученных ГЭЦ-содержащих композитов были охарактеризованы методами ИКС, сканирующей и просвечивающей электронной микроскопии. Полученные данные подтвердили закрепление полимера на поверхности носителя.

Проведены исследования по изучению сорбционной активности разработанных ГЭЦ-силикатных композитов по отношению к ионам Pd²⁺. Содержание палладия в составе разработанных композитов уменьшалось с увеличением количества ГЭЦ: 0,9% Pd-БТ/ ГЭС (4%), 0,8% Pd-БТ/ГЭЦ (9%), 0,6% Pd-БТ/ГЭЦ (19%). Для сравнения активности и селективности композитов с различным содержанием ГЭЦ были приготовлены катализаторы с одинаковым содержанием палладия (0,6%).

Разработанные палладиевые катализаторы показали активность в реакции гидрирования фенилацетилена при температуре 40°C и атмосферном давлении водорода. Наибольшей эффективностью и активностью обладает 0,6% Pd-БТ/ГЭЦ композит с содержанием ГЭЦ 9%, селективность на котором по стиrolу составила 92,0% при 96,4% конверсии субстрата.

Ключевые слова. 2-Гидроксиэтилцеллюлоза, полисахариды, бентонит, каталитическая активность, гидрирование, палладиевые катализаторы.

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