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**SYNTHESIS AND CATALYTIC PROPERTIES OF SUPPORTED  
POLYACRYLAMIDE-STABILIZED Pd-Ag CATALYSTS**

**Abstract.** Low-percentage mono- and bimetallic polyacrylamide-stabilized Pd and Ag nanoparticles fixed on the surface of zinc oxide have been synthesized. Catalysts without treatment of zinc oxide with polymer have been prepared to determine the effect of polyacrylamide on the catalytic properties of palladium and silver monometallic systems. Preliminary treatment of inorganic oxide with polyacrylamide leads to an increase in the dispersion of palladium particles. The formation of palladium and silver nanoparticles on the surface of zinc oxide have been confirmed by transmission electron microscopy. A palladium catalyst stabilized with PAA is characterized by the formation of fine metal particles with a size of 10-15 nm. The catalytic activity of polymer-stabilized mono- and bimetallic catalysts in the hydrogenation of 2-propyn-1-ol and propen-2-ol-1 at 40°C and atmospheric pressure of hydrogen have been studied. The obtained bimetallic catalyst during the hydrogenation of alkynol to alkenol exhibits high activity and a selectivity of 97.0% with a conversion of 98.6%. The resulting propen-2-ol-1 was hydrogenated to propanol on palladium-silver catalyst, in contrast to the processes occurring in the presence of a monometallic palladium catalyst. Analysis of the results confirms that the bimetallic catalyst is optimal, at which the reaction rate and selectivity for the alkenol are maximal. The introduction of silver helps to suppress a significant increase in selectivity.

**Key words:** polymer-metal complexes, bimetallic catalyst, hydrogenation, 2-propyn-1-ol, palladium catalysts.

**Introduction**

In recent decades, a significant interest of researchers working in the field of catalysis is aimed at the design of new types of catalysts that have high activity, selectivity and stability. Approaches used in nanotechnology, materials science, achievements in macromolecular and coordination chemistry, many other branches of knowledge are used for these purposes. Thus, the structure, size and homogeneity of the supported active phase are of great importance for the catalysts most demanded in industry [1-4]. Reducing the particle size contributes to an increase in the number of catalytic sites involved in the process, and, consequently, to an increase in the activity of the catalyst with a low metal content. In recent years, polymers with various functional groups have been actively used to create such systems. Their main functions are stabilization of metal nanoparticles, fixation of the latter on the surface of supports.

Various approaches in the creation of such catalysts are presented in the literature [5-8]. In many cases, the nanoscale metal particles are formed on the surface of the supports in the preparation of supported catalysts, their further calcination and reduction, the polymer, as a rule, not involved in the catalytic process as part of the active phase. These works are mainly devoted to palladium catalysts. At the same time, interest in gold and silver nanoparticles has increased with the development of nanotechnology. There have appeared papers on their application in catalytic processes [9-10].

We have developed a simple and sufficiently reliable method of preparation of polymer-metal catalysts fixed on oxides [11-12], consisting in the sequential adsorption of functional polymers, and then the metal on the surface of the oxides. High catalytic activity of such palladium and nickel catalysts in the

hydrogenation reaction was demonstrated. In this paper, we consider the methods for the preparation of bimetallic palladium-silver catalysts for the hydrogenation of 2-propyn-1-ol as a model compound.

### Experimental

**Reagents.** The 2-Propyn-1-ol of chemically grade was purified by distillation, the purity was determined by chromatography. The ethanol (reagent grade),  $\text{PdCl}_2$  (reagent grade),  $\text{HCl}$  (reagent grade,  $\rho = 1.19 \text{ g/cm}^3$ ),  $\text{AgNO}_3$  (pure for analysis) and polyacrylamide ( $M_w = 500 \text{ kDa}$ , "Sigma Aldrich") were used without further purification. The zinc oxide (reagent grade) with a specific surface area of about  $10.2 \text{ m}^2/\text{g}$  was used as an inorganic support.

**Preparation of 1%Pd-PAA/ZnO, 1%Ag-PAA/ZnO and 1%Pd-Ag(3:1)-PAA/ZnO catalysts.** The catalysts were prepared by the adsorption method according to the procedure proposed in [13]. An aqueous solution of polymer (5 ml) containing 0.0067 g of PAA was added to the aqueous suspension of the support (1 g of zinc oxide in 5 ml of water) by dropping. The mixture was stirred continuously for 2 hours at room temperature. The amount of used polymer to prepare the catalyst was taken from a calculation of one transition metal atom per one macromolecular unit. Then, to the suspension of the polyacrylamide-modified zinc oxide were added a solution of palladium chloride (silver nitrate) (5ml) dropwise, which contains 0.0101g of metal(s) and the mixture was further stirred for 3 hours until the metal was completely bound with polymer-modified system. The obtained catalysts kept in the mother liquor for 16 hours and then were washed with distilled water and dried in air.

In the case of obtaining bimetallic systems, metals were supported sequentially - first silver, then palladium. The amount of metals was taken from a calculation for the preparation of 1% catalysts with the ratio of metals  $\text{Pd:Ag} = 3:1$ .

**The analysis of catalysts.** The extent of attachment of the components was determined by the difference of metal ions concentration in mother liquor before and after sorption. The palladium ions concentration was determined on an SPh-2000 spectrophotometer at wavelength  $\lambda_{\text{Pd}} = 410 \text{ nm}$ . The silver ions concentration was determined on an ANION-4100 ionometer using ion-selective electrodes (Elis131Ag, Elis131Cu). The ionometer was calibrated using a series of standard solutions of silver nitrate with a concentration of  $10^{-2}$ - $10^{-7} \text{ mol/l}$ . Analysis of mother liquors after sorption showed that the supported metals amount is about 99.0%.

The electron-microscopic studies were performed on a "EVO 50 XVP" (Carl Zeiss) scanning electron microscope (SEM).

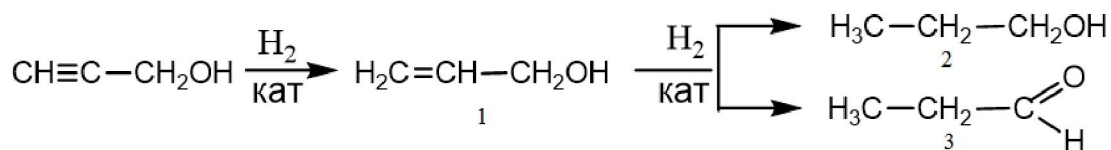
TEM (transmission electron microscopy) patterns of samples were obtained on a JEM-1011 transmission electron microscope with a Morada (OLYMPUS) CCD-digital camera from Geol (Japan) by method of suspensions.

**Hydrogenation of 2-propyn-1-ol.** Hydrogenation were carried out in thermostatic glass vessel with constant shaking (600-700 oscillations per minute). The reaction was carried out in ethanol (20ml) at  $40^\circ\text{C}$  and atmospheric pressure of hydrogen. The weight of the catalyst was 0.05 g. Catalysts were treated with hydrogen during 0.5 hour before reactant was added into the reactor. The substrate concentration was 0.11 mol/l. The volume of the introduced substrate calculated for the absorption of 100 mL hydrogen. The reaction rate was calculated from the change of hydrogen absorption per unit time.

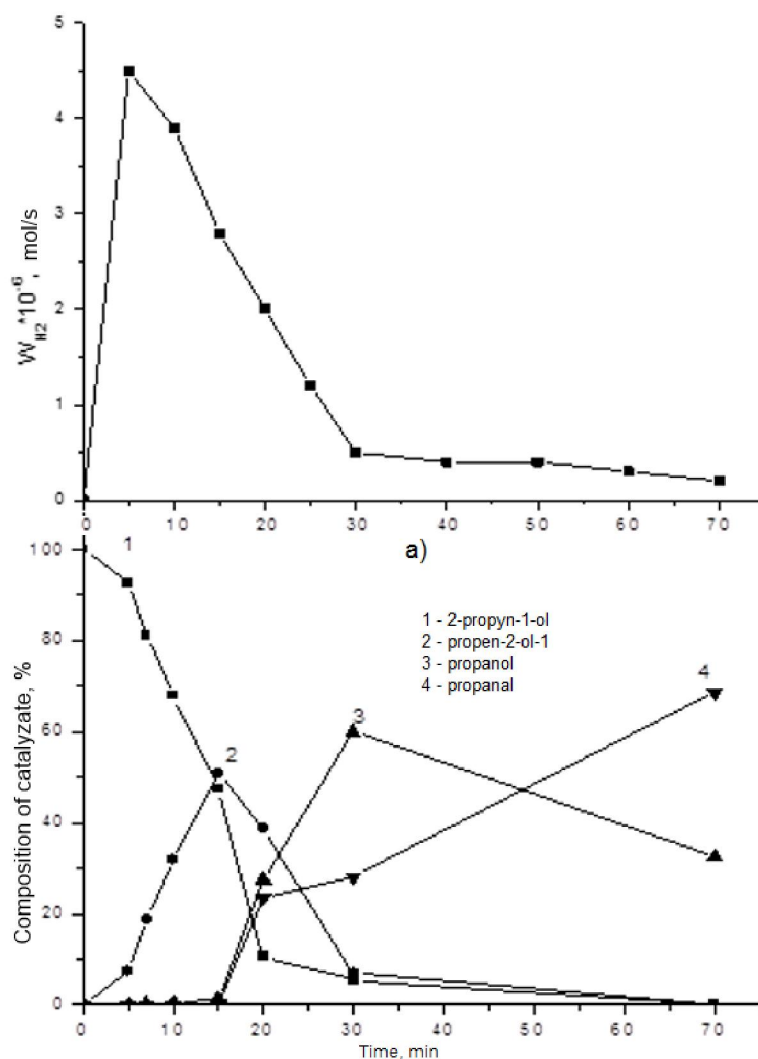
The analysis of hydrogenation products was carried out on Khromos GKh-1000 ("Khromos", Russia) using a flame ionization detector in an isothermal mode and a capillary column BP21 (FFAP) with 50 m length and 0.32 mm inner diameter polar phase (PEG modified with nitroterephthalate). The column was maintained at  $90^\circ\text{C}$ , the temperature in the evaporation chamber was  $200^\circ\text{C}$ . Helium was used as a carrier gas. The sample volume was set to 0.2  $\mu\text{l}$ . Reaction mixture samples were taken 4-5 times during the experiment. The selectivity of the catalyst was defined as the proportion of the main product among all reaction products at a given conversion rate.

### Results and discussion

Hydrogenation of 2-propyn-1-ol is carried out with formation of propene-2-ol-1 (1) and the latter is converted into the propanol (2). Depending on the nature of the catalyst also may be formed propanal (3) [14-17]:



The palladium catalyst was shown high activity in the first minutes of the reaction (Figure 1, a). However, the reaction rate on it decreases from  $4.5 \cdot 10^{-6}$  mol/s to  $0.5 \cdot 10^{-6}$  mol/s and remains so until 70 minutes.



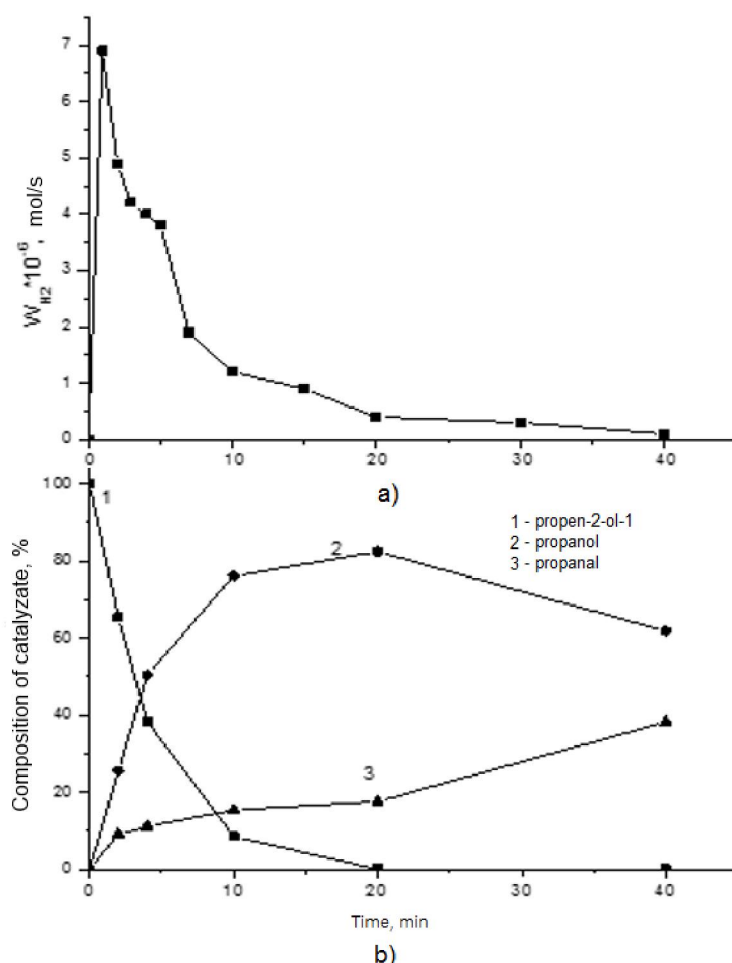
Experimental conditions: catalyst weight 0.05 g, temperature 40°C, pressure  $\text{H}_2$  0.1 MPa, solvent - ethyl alcohol

Figure 1 – Rate (a) and the diagram of the composition of formed reaction products (b) of the hydrogenation of 2-propyn-1-ol on 1%Pd-PAA/ZnO catalyst

According to the chromatographic analysis, the maximum yield of propen-2-ol-1 was reached by 1%Pd-PAA/ZnO at 52% conversion of alkyne-2-ol-1 (Figure 1, b). The propanol, the amount of which reaches 60%, was rapidly accumulated in the reaction products, and then gradually decreases.

The rate of formation of propanal increases after the full conversion of the olefinic alcohol to the reaction products (curve 2). This is probably due to the isomerization of propen-2-ol-1 to propanal (migration of the double bond) or to the dehydrogenation of the resulting propanol, decrease of the content of this in the reaction products and a significant slowdown of the process indicates this.

Hydrogenation of propen-2-ol-1 on 1%Pd-PAA/ZnO have been carried out in comparison (Figure 2). The reaction rate drops sharply from the first minutes. The process ends with the full conversion of the alkenol to the reaction products.



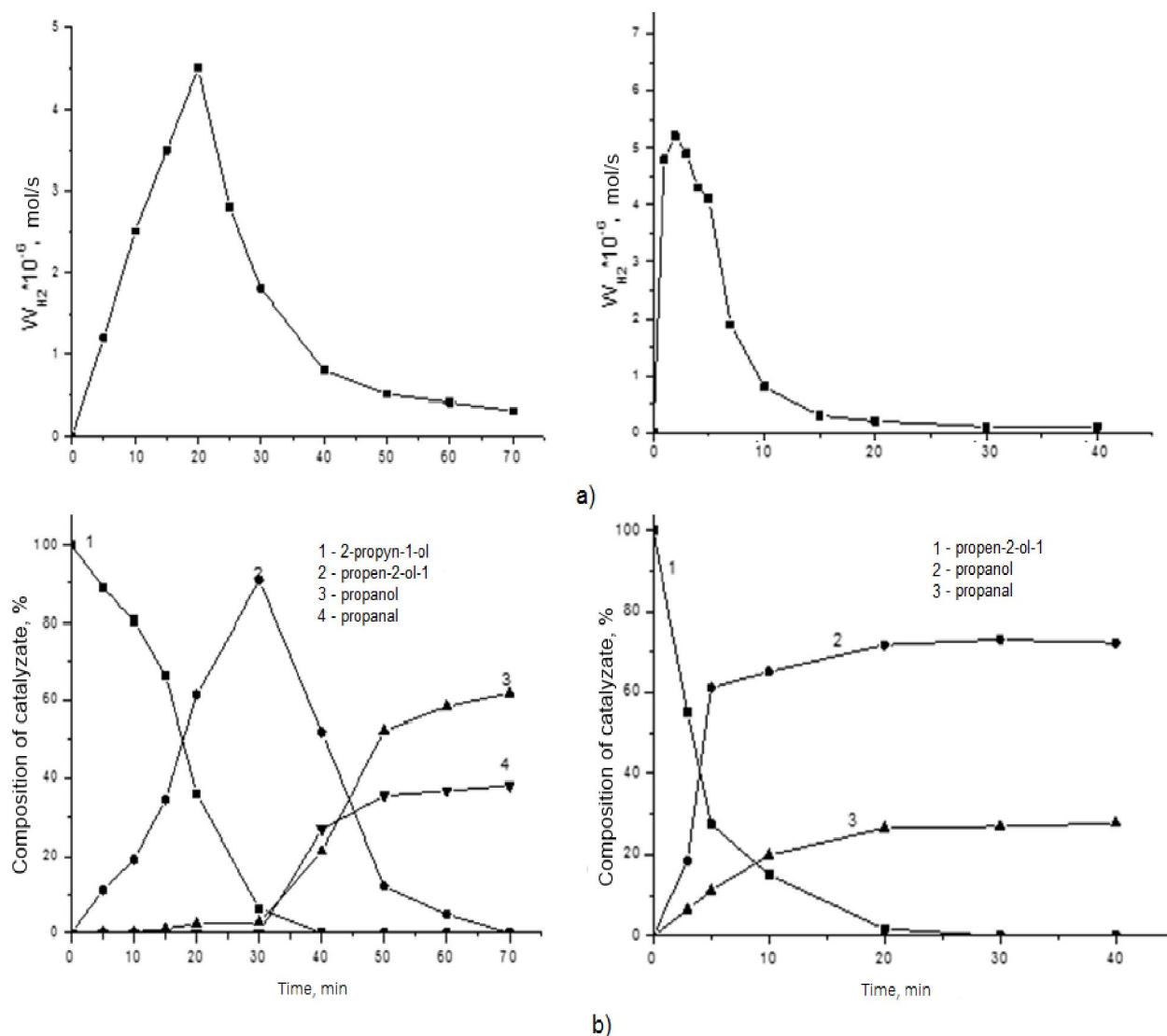
Experimental conditions: catalyst weight 0.05 g, temperature 40°C, pressure  $H_2$  0.1 MPa, solvent - ethyl alcohol

Figure 2 – Rate (a) and the diagram of the composition of formed reaction products (b) of the hydrogenation of propen-2-ol-1 on 1%Pd-PAA/ZnO catalyst

It should be noted that, as in the case of hydrogenation of propen-2-ol-1, formed during the reduction of 2-propyn-1-ol, propanol predominantly accumulates in the reaction products, the amount of which decreases after complete conversion of the initial alkynol, and the propanal increases. (Figure 2, b).

It should be noted that, the propanol is mainly accumulated as in the case of hydrogenation of propen-2-ol-1, formed during the reduction of 2-propyn-1-ol in the reaction products. The amount of propanol decreases after full conversion of the initial alkynol, and the propanal increases (Figure 2, b).

The rate of hydrogenation of 2-propyn-1-ol increases gradually when silver was added to the catalyst composition in the ratio Pd:Ag = 3:1 and reaches the maximum value ( $4.5 \cdot 10^{-6}$  mol/s) after ~ 25 minutes after the reaction initiation, and then falls sharply (Figure 3, a). According to chromatographic analysis, at this time, the reaction medium was observed accumulation of substantially only the olefinic alcohol – 2-propen-1-ol (Figure 3, a). I.e. the selective hydrogenation of alkyne to alkenol occurs, the yield of which on this catalyst reaches 87.2%, and then sharply decreases, which is associated with the formation of both propanol and propanal as the reaction product. The resulting propen-2-ol-1 was hydrogenated to propanol on palladium-silver catalyst, in contrast to the processes occurring in the presence of a monometallic palladium catalyst. This catalyst does not show a decrease in propanol content. It can be assumed that propen-2-ol-1 is predominantly isomerized to the aldehyde.



Experimental conditions: catalyst weight 0.05 g, temperature 40°C, pressure  $H_2$  0.1 MPa, solvent - ethyl alcohol

Figure 3 – Rates (a) and the diagrams of the composition of formed reaction products (b) of the hydrogenation of 2-propyn-1-ol and propen-2-ol-1 on 1%Pd-Ag(3:1)-PAA/ZnO catalyst

When hydrogenating propene-2-ol-1 (Figure 3, b), the course of the kinetic curve, also the change in the composition of the reaction mixture in time, almost completely corresponds to the results obtained during the hydrogenation of 2-propyn-1-ol starting from 25-30 minutes, when the alkanol was completely converted to alkenol.

Thus, the correlation between the change in the composition of the reaction mixture and the rate of the hydrogenation reaction of both the tested alkyne and the alkenol on all the studied catalysts was found.

The hydrogenation of 2-propyn-1-ol on synthesized catalysts is presented in Table 1. The catalysts have been prepared without polymer treatment with zinc oxide to determine the effect of polyacrylamide on the catalytic properties of palladium and silver monometallic catalysts. It was found that the introduction of polyacrylamide in the catalysts leads to a significant improvement in their catalytic properties. Thus, the reaction rate on palladium and silver catalysts without a polymer is more than 2-4 times lower than for similar polymer-containing catalysts. The yield of propen-2-ol-1 and, accordingly, the selectivity of the process were increased. The reaction rate is low on both monometallic silver catalysts and the process spontaneously stops. The maximum conversion did not exceed 11%. At the same time, propanal did not form on the silver catalyst (Table 1).



Analysis of the results confirms that the bimetallic catalyst is optimal, at which the reaction rate and selectivity for the alkenol are maximal. The introduction of silver helps to suppress the isomerization process and a significant increase in selectivity, which is consistent with the data in [18-19].

Table 1 – Hydrogenation of 2-propyn-1-ol in the presence of one-percent monometallic Pd, Ag and bimetallic Pd-Ag catalysts

Catalysts	Reaction rate, $W \cdot 10^{-6}$ , mol/s	Composition of catalyzate, %			Selectivity of C=C, %
		propen-2-ol-1	propanol	propanal	
Pd /ZnO	2.1	34.6	13.4	7.5	62.3
Pd-PAA/ZnO	4.5	50.8	1.4	0.4	96.6
Ag /ZnO	0.3	8.7	2.3	0	79.9
Ag-PAA/ZnO	1.2	9.2	1.5	0	86.0
Pd-Ag(3:1)-PAA/ZnO	4.5	95.7	2.8	0.1	97.0
Conditions: T= 80°C; P = 1atm; $m_{\text{kat}} = 0.05\text{g}$ ; solvent - $\text{C}_2\text{H}_5\text{OH}$					

The increase in activity and selectivity of catalysts in the modification of their polyacrylamide is probably due to the formation of a layer of polymer with embedded particles of the active phase (palladium, silver or their mixture) on the zinc oxide surface, which was confirmed by electron microscopy.

Thus, when comparing the photomicrographs of 1%Ag/ZnO and 1%Ag-PAA/ZnO samples obtained by scanning electron microscopy (SEM), it was found that the aggregates in the form of thin coiled needle-like films of the polyacrylamide compound with silver ions was formed on the PAA-modified surface of ZnO in contrast to a catalyst without a polymer (Fig. 4, b).

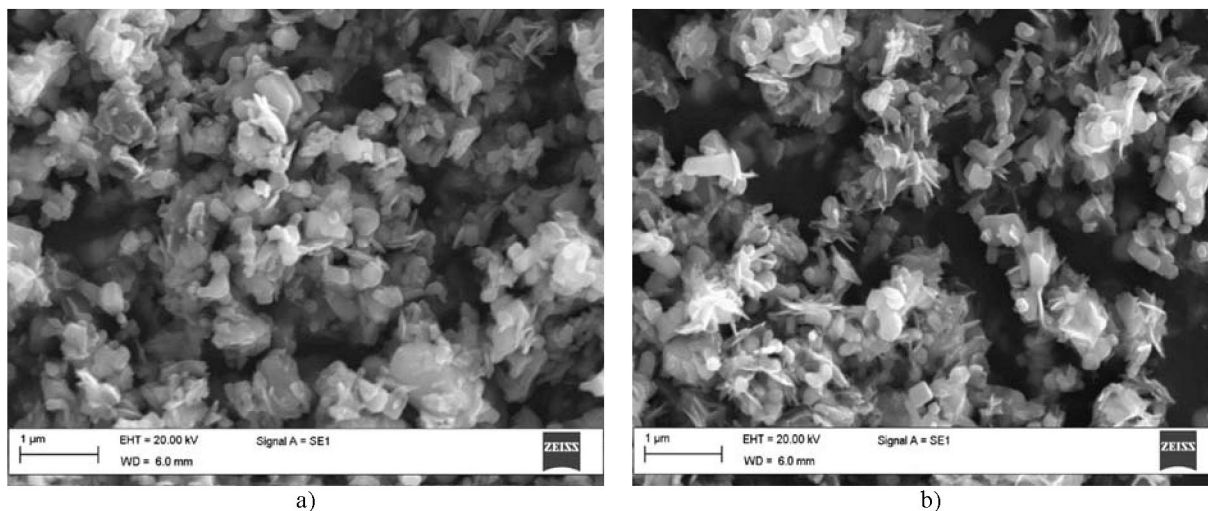


Figure 4 - Micrograph (SEM) of 1% Ag/ZnO (a) and 1%Ag-PAA/ZnO (b)

The formation of the polymer-metal complex on the surface of zinc oxide was confirmed by transmission electron microscopy (TEM). Thus, the polyacrylamide film with impregnations of silver nanoparticles (30-40 nm) uniformly distributed in the polymer matrix was observed on a microphotography of 1%Ag-PAA/ZnO catalyst (Fig. 5).

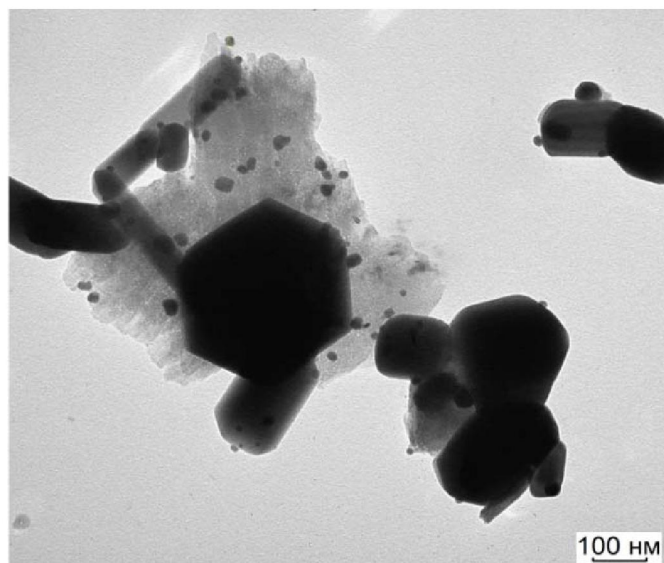


Figure 5 - Micrograph (TEM) of 1% Ag-PAA/ZnO

A palladium catalyst prepared with the participation of PAA is also characterized by the formation of fine metal particles with a size of 10-15 nm, which uniformly covered the surface of the support (Figure 6).

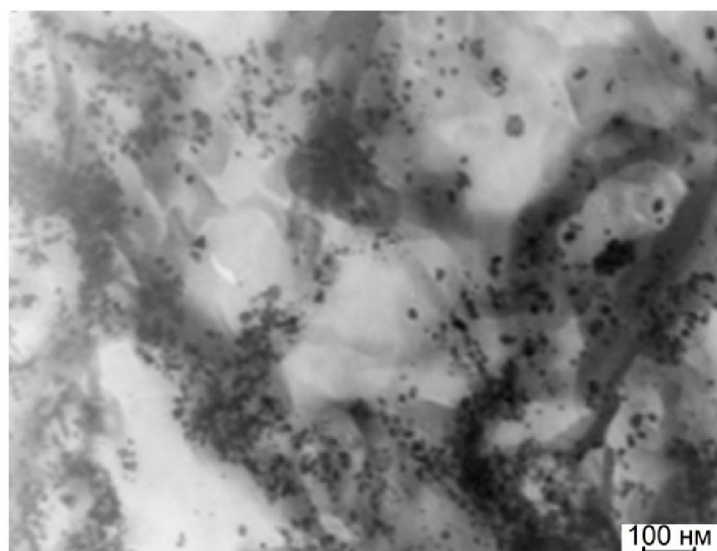


Figure 6 - Micrograph (TEM) of 1% Pd-PAA/ZnO

Earlier, we showed that in the polymer-free system obtained by supporting an aqueous solution of palladium chloride to zinc oxide, the active phase of the catalyst is a particle size of 30-35 nm, which is quite randomly distributed on the surface of zinc oxide [20]. Thus, pretreatment of inorganic oxide with polyacrylamide leads to an increase in the dispersion of palladium particles, which is probably due to complexation and stabilization of palladium by polyacrylamide.

The bimetallic catalyst was characterized by the formation of active phase particles with sizes of 30-40 nm, as in monometallic silver (Figure 7). Probably, both metals enter into the composition of such particles, since during the hydrogenation of 2-propyn-1-ol in propen-2-ol-1 showed the highest selectivity on these catalysts.



Figure 7 - Micrograph (TEM) of 1%Pd-Ag(3:1)-PAA/ZnO

According to the data of [21-22], bimetallic clusters are formed on the surface of the catalyst by successive deposition of palladium and then silver onto supports, followed by their calcination and reduction; they are possibly responsible for the selective hydrogenation of acetylene to ethylene. It is possible to form nanoparticles by the Core-Shell type [23] with the use of polymer-stabilizer.

Thus, the method for the preparation of polyacrylamide-stabilized palladium-silver catalyst on zinc oxide has been developed. The obtained composite exhibits high activity and selectivity in the hydrogenation of 2-propyn-1-ol to propen-2-ol-1 with the yield of the desired product of 95.7% and 97% selectivity. High-temperature stages of calcination and reduction are eliminated in the preparation of the catalyst, which greatly simplifies the procedure for their synthesis.

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