

The change in the conformations of macromolecules with a change in the properties of the environment plays an important role in biological and catalytic processes. In appropriate solvents polymer chains are stretched toward the solvent, whereas in inappropriate solvents they take the form of folded globules.

Schematically the catalyst formation can be represented as follows. During the interaction of  $\text{PdCl}_4^{2-}$  with the polymer fixed on the oxide nanoparticles with sizes of 4-6 nm surrounded by polymer chains are formed. The interaction of the external hydrophobic parts of polymer leads to the formation of agglomerates containing three, four or more palladium nanoparticles (Fig. 4).

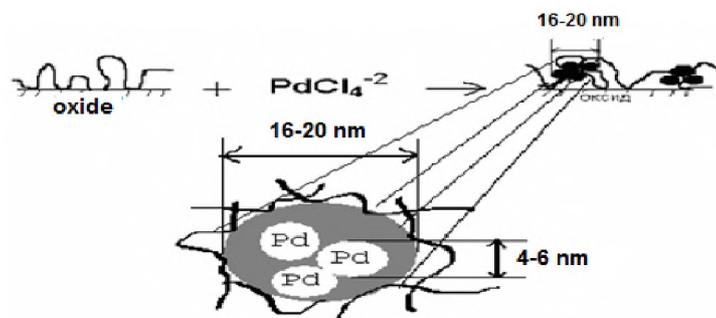


Figure 4. Scheme of formation of a polymer-palladium complex on the surface of carrier.

To reduce the surface density and viscosity as well as to increase the mass transfer rate catalytic processes must be carried out in the presence of a solvent. The use of solvents in catalytic hydrogenation provides the removal of heat from the exothermic reaction, facilitates the reduction of catalyst and in some cases significantly affects selectivity and rate of hydrogenation.

In order to study the effect of solvent nature on the catalytic properties of polymer-containing catalysts, hydrogenation of  $\text{C}_{15}$  acetylene alcohol was carried out over 1% Pd-PEG/ZnO and 1% Pd-PVPD/ZnO in ethanol and water medium (Table 2).

Table 2. Influence of the nature of solvent on the characteristics of 1% Pd-PVPD/ZnO and 1% Pd-PEG/ZnO catalysts ( $m = 0.05$  g) in the process of 3,7,11-trimethyldodecin-1-ol-3 hydrogenation ( $T = 313\text{K}$  and  $P_{\text{H}_2} = 0.1$  MPa)

Catalyst	Medium	$W \cdot 10^{-4}$ , mole/l·sec		$S_{\text{C}=\text{C}}$ , %	TON
		$\text{C}\equiv\text{C}$	$\text{C}=\text{C}$		
1%Pd-PVPD/ZnO	Ethanol	27,97	0,04	98	62000
1%Pd- PVPD/ZnO	Water	14,57	0,05	92	12000
1%Pd-PEG/ZnO	Ethanol	6,23	0,08	96	3800
1%Pd- PEG/ZnO	Water	17,69	0,12	98	10000

Activity, selectivity, and stability of 1% Pd-PVPD/ZnO catalyst in ethanol ( $W = 27.97 \cdot 10^{-4}$  mole / l sec;  $S = 98\%$ ; TON = 62000) is higher than in water ( $W = 14.57 \cdot 10^{-4}$  mole / l sec;  $S = 92\%$ ; TON = 12000).

It is known that PVPD is readily soluble in both water and ethanol, that is fixed on zinc oxide polymer-metal complexes are in a swollen state, and active sites are available to activate unsaturated compounds. The lower activity of catalyst in water is explained by the insolubility of compound to be hydrogenated in it.

Hydrogenation rate over 1% Pd-PEG/ZnO catalyst in water medium is 3 times higher than in ethanol. For polyethylene glycol water is appropriate and ethanol is inappropriate solvent. As a result, the fixed Pd-PEG complexes swell in water, which leads to the formation of incoherent ravel on the carrier surface, and the active metal centers inside the polymer-metal complexes become available for activation. In ethanol Pd-PEG systems are compressed into globules, which makes it difficult to carry out the catalytic process.

Thus, the hydrogenation of  $\text{C}_{15}$  acetylene alcohol is most effective over 1% Pd-PVPD/ZnO catalyst in an ethanol medium in which the hydrogenated compound is soluble and the polymer complex is in the most favorable for its activation state.

High activity, selectivity and stability of polyvinylpyrrolidone complexes of palladium supported on zinc oxide, availability and relatively low cost of PVPD and ZnO, as well as low concentration of expensive palladium provide the prospects of using this catalyst on an industrial scale for the hydrogenation of long chain acetylene compounds in order to obtain biologically active substances.