Polymer-stabilized mono- and bimetallic catalysts for hydrogenation under mild conditions

Assemgul Auyezkhanova,* Alima Zharmagambetova, Kuralay Seitkaliyeva, Akmaral Darmenbayeva

D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry, Almaty, 050010, Kazakhstan
Corresponding author: +7(727)2915722, e-mail: a.assemgul@mail.ru

Abstract: Polymer-stabilized monometallic (Pd- and Ag-) and bimetallic (Pd:Ag-3:1) catalysts supported on zinc oxide have been synthesized by the polyol method. The active phase has been stabilized by the polyacrylamide (PAA) fixed on the support. It has been shown that bimetallic 1%Pd-Ag(3:1)-PAA/ZnO is an active, selective and stable catalyst for the liquid-phase hydrogenation of phenylacetylene to styrene at atmospheric pressure of hydrogen and at a temperature of 40°C. The nature of the reducing agent has been varied. As a reducing agent, natural glucose, ethylene glycol, potassium-sodium tartrate were chosen. It has been established that glucose is the optimal reducing agent for the preparation of polyol Pd-Ag catalysts.

Keywords: hydrogenation, polymer-stabilized catalysts, phenylacetylene.

1. Introduction

In recent years, one of the most common ways of the creation of polymer-stabilized catalytic systems with metal nanoparticles is their subsequent reduction by liquid or gaseous inorganic compounds, and polyhydric alcohols (polyol method) [1-3]. In this paper, data on the study of catalytic properties of polyacrylamide-stabilized silver and palladium nanoparticles synthesized by the polyol method in the hydrogenation of phenylacetylene are presented.

2. Experimental

Preparation of PAA-stabilized mono- and bimetallic catalysts. Low-percentage (up to 1 wt.%) polymer-stabilized monometallic (Pd and Ag) and bimetallic Pd-Ag (Pd:Ag - 3:1) catalysts supported on the zinc oxide were synthesized by the polyol process.

Natural glucose monosaccharide, ethylene glycol, potassium-sodium tartrate were chosen as reducing agents. The reduction of metals was carried out at a temperature of 80°C for 30 minutes. The catalysts were prepared by sequentially adsorption of the polymer to the surface of zinc oxide, and then the active phase (Pd and Ag) was added.

Hydrogenation of phenylacetylene (PhA). Hydrogenation was carried out in thermostatic glass vessel in ethanol (20ml) at 40°C and atmospheric pressure of hydrogen with constant shaking.

The analysis of hydrogenation products was carried out on Khromos GKh-1000 (“Khromos”, Russia) with 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). Helium was used as a carrier gas. The sample volume was set to 0.2 μl. Reaction mixture samples were taken 4-5 times during the experiment.

3. Results and discussion

The obtained PAA-stabilized Pd-, Ag-, and Pd-Ag nanoparticles deposited on zinc oxide were tested in liquid-phase hydrogenation of phenylacetylene at a temperature of 40°C and atmospheric hydrogen pressure and showed high selectivity for styrene.

In the presence of the bimetallic PAA-stabilized catalyst supported on ZnO, a 100% conversion and maximum selectivity for styrene were observed (Table 1). The stability of the catalyst also increases, it is characterized by the number of catalytic acts on one metal atom (TON - turnover number). The 1%Ag-PAA/ZnO was not tested for stability due to the low reaction rates.

Table 1. Hydrogenation of phenylacetylene in the presence of 1% mono- (Pd-, Ag-) and bimetallic (Pd-Ag) catalysts prepared by the polyol method.

Catalysts	$W \cdot 10^{-6}$ mol/s	Selectivity, %		Conversion, %	Stability, TON
		styrene	ethylbenzene		
1%Pd-PAA/ZnO	7.6	85.0	15.0	100.0	3255
1%Pd-Ag(3:1)-PAA/ZnO	5.9	97.3	27.0	100.0	9300
1%Ag-PAA/ZnO	0.2	86.2	13.8	4.7	-

The comparison of properties depending on the reducing agent at the optimal 1%Pd-Ag (3:1)-PAA/ZnO catalyst showed that the selectivity for styrene decreases from 97.3% to 86.0% in the range glucose → ethylene glycol → potassium sodium tartrate. The conversion of phenylacetylene in this series also decreases (Figure 1).

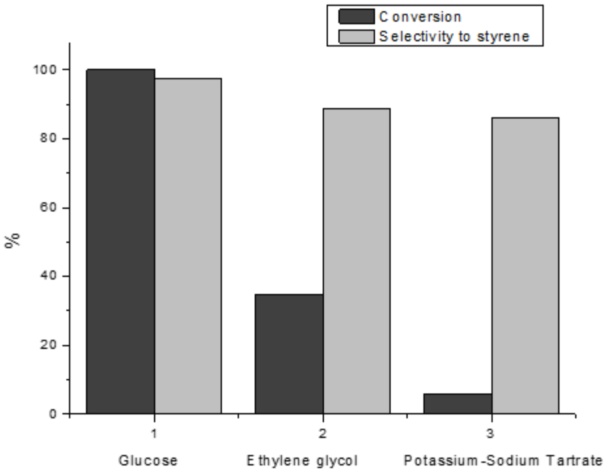

Figure 1. Hydrogenation of phenylacetylene on a bimetallic 1% Pd-Ag (3:1)-PAA / ZnO catalyst prepared by a polyol process with various reducing agents

4. Conclusion

Thus, it has been shown that the optimal reducing agent for the polyol preparation of Pd-Ag catalysts is glucose. This catalyst is the most active ($W = 5.9 \cdot 10^{-6}$ mol/s, substrate conversion 100%) and selective for styrene (97.3%). The obtained catalysts were studied by electron microscopy and IR-spectroscopy. The obtained data indicates the interaction between the components of the catalysts and the fixation of the polymer and the active phase on the surface of support.

References

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