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Selective Hydrogenation of Pyridine and Derivatives of It on Bimetallic Catalysts

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Abstract—A study is performed of the catalytic properties of bimetallic nanoparticles based on palladium and a base metal (silver or copper) in the selective hydrogenation of pyridine and derivatives of it with the formation of piperidine and derivatives of it. It is established that the effect of increasing the activity of bimetallic nanoparticles is associated with the small size of particles (2–3 nm), relative to monometallic palladium catalyst. The conversion of pyridine reaches 99% with a piperidine selectivity of 99% under mild conditions (60°C, pressure $H_2 = 70$ atm).

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INTRODUCTION

Developing efficient catalytic systems for processing raw materials containing nitrogenous heterocyclic compounds and a way of processing pyridine and derivatives of it into such valuable products as hydrogenated heterocyclic compounds is of great practical importance [1–4]. As a product of pyridine hydrogenation and derivatives of it, piperidine is in demand for the production of drugs and other valuable products, and recently as a compound for obtaining ionic liquids and materials for hydrogen storage [5–8]. Pyridine and derivatives of it are freely available compounds obtained during the processing of coal and petroleum products via, e.g., the cyclization of acetylenic compounds with the participation of ammonia.

The hydrogenation of unsaturated compounds is catalyzed by noble metals deposited on supports with developed specific surface areas [9–29]. Homogeneous catalysts and metal complexes based on noble metals are used for the hydrogenation of pyridine and derivatives of it, but a major drawback is the difficulty of separating them from the reaction medium (product) and the impossibility of reuse. The familiar way of hydrogenating pyridine and derivatives of it using catalysts containing cobalt nanoparticles is the only example of using non-noble metals in the catalytic hydrogenation of pyridine and derivatives of it [30]. A disadvantage of this technique is the insufficiently high stability of the catalyst, which loses its activity in several successive cycles due to sintering and the coarsening of cobalt nanoparticles.

The heterogeneous catalytic hydrogenation of pyridine and derivatives of it is mainly done using catalysts based on noble metals [31]. Catalysts based on ruthenium (2.5 wt %) on a nitrogen-doped mesoporous carbon support were studied in [32] for the hydrogenation of quinoline at 40°C and 10 atm H_2. The turnover frequency for this catalyst (TOF) was 71.0 h^{-1}. Rh- and Ru-catalysts display high activity only when the content of the noble metal is at least 10 wt % [33].

A large number of different mono-, bi-, and trimetallic catalysts (more than 70 systems) on oxide supports have been tested in the hydrogenation of pyridine and quinoline [34].

Rhodium nanoparticles ~1.5 nm in size supported on aluminum oxide are also active in pyridine hydrogenation [35]. Pd/C-, Pt/C-, and Rh/C-catalysts with high contents of metals have been studied in the hydrogenation of pyridines with hydrogen released through the membrane during the in situ electrolysis of water (30–80 atm, 60–80°C) [36, 37]. However, the performance of the system is very low because the rate of hydrogenation is determined by that of the delivery of hydrogen to the catalyst placed on the surface of the cartridge. The most efficient way of hydrogenating pyridines is using carbon-supported palladium catalysts, the properties of which have been studied in the hydrogenation of arylpyridines of various structures [38]. The maximum selectivity for phenylpiperidine in the hydrogenation of phenylpyridine was 96% with 87% conversion of the latter.

Table 1. Results from testing catalysts in the reaction of pyridine hydrogenation with the participation of catalysts Pd, Pd–Ag, and Pd–Cu nanoparticles supported on alumina (60°C, pressure $H_2 = 70$ atm)

Catalyst	Pyridine conversion, %	Selectivity by piperidine, %
1% Pd/Al_2O_3 (sample comparison)	85	87
0.5% Pd–1% Ag/Al_2O_3	99	99
0.5% Pd–1% Cu/Al_2O_3	97	99

Table 2. Results from testing catalysts in the hydrogenation of heterocyclic compounds with the participation of nanoparticle catalyst Pd–Ag deposited on aluminum oxide (60°C, pressure $H_2 = 70$ atm)

Heterocyclic compound	Conversion of heterocyclic compound, %	Selectivity for fully hydrogenated compound, %
2-Hydroxyethylpyridine	98	97
2,4-Lutidine	99	99
2-Methylquinoline	99	99
1-Pyrrolidinocyclopentene-2	98	98
n-Isopropylindole	97	96
Indole	99	99

It should be noted that most known catalysts of the hydrogenation of unsaturated compounds, including the catalysts listed above, are easily poisoned by nitrogen compounds [39] and are very expensive, since they contain considerable amounts of expensive metals (from 2 to 10 wt %).

It is known that using hybrid or composite materials produces a synergistic effect [40–49]. Synergistic effects are also observed for bimetallic systems, which in some cases allows us to achieve better dispersion of the active metal and improve activity in catalytic processes. The use of bimetallic catalysts containing nanoparticles of palladium and a second metal (copper, silver) deposited on alumina thus allows us to conduct the process more efficiently.

The aim of this work was to create an efficient catalyst for the hydrogenation of pyridine and derivatives of it that allows us to improve the selectivity of the process while maintaining high conversion of the heterocyclic compound, lower the cost of the process by reducing that of the catalytic system, and increase the stability of the catalyst in successive cycles of the hydrogenation of pyridine and derivatives of it.

EXPERIMENTAL

Catalysts were prepared using γ-alumina with a specific surface area of 180 m^2/g (Ryazan refinery). Copper or silver (1 wt %) was applied to alumina preliminarily dried for 2 hours in air at 100°C by impregnating it with an aqueous solution of copper or silver nitrate, followed by drying for 2 h at 100°C and calcination for 2 h in a stream of air at 300°C and reduction in a stream of hydrogen for 2 h at 300°C. Palladium (0.5 wt %) was applied via precipitation using $PdCl_2$, with subsequent drying for 2 h at 100°C and hydrogen treatment at 200°C. The selective hydrogenation of pyridine and derivatives of it was performed under isothermal conditions in a shaking reactor at 60°C on catalysts containing Pd nanoparticles (a reference catalyst), Pd–Ag, and Pd–Cu supported on alumina.

RESULTS AND DISCUSSION

A catalyst for the hydrogenation of pyridine and derivatives of it was proposed that contained bimetallic palladium–copper or palladium–silver nanoparticles with an average size of 2–3 nm on a support of aluminum oxide. The content of palladium was 0.5 wt % (i.e., 2–10 times lower than in systems known from the literature). It should be noted that there are no examples in the literature or patents illustrating the use of bimetallic nanoparticles deposited on alumina for the hydrogenation of pyridine and derivatives of it.

The synthesized bimetallic catalysts supported on aluminum oxide are characterized by a higher activity in the selective hydrogenation of pyridine and derivatives of it with molecular hydrogen compared to the monometallic catalyst supported on aluminum oxide (Table 1). Palladium metal particles are responsible for the activation of pyridine and derivatives of it and the activation of hydrogen. Thus, Pd–Cu and Pd–Ag particles exhibit a synergistic effect in the selective hydrogenation of pyridine and derivatives of it.

Maximum activity in the liquid-phase hydrogenation of pyridine and derivatives of it (60°C, pressure $H_2 = 70$ atm) was observed for a catalyst with a supported bimetallic nanoparticle size of 2–3 nm. This relationship is explained by the presence of low-coordinated palladium atoms, which serve as active centers for hydrogen activation and adsorption of the heterocyclic compound. The higher activity of the catalysts modified with silver and copper is also explained by the higher dispersity and small particle size of palladium, which is confirmed by the data of X-ray phase analysis and electron microscopy: particle sizes are 2–3 nm for modified catalysts and 5–10 nm for unmodified catalysts.

We studied the hydrogenation of other heterocyclic compounds, including 2-hydroxyethylpyridine, 2,4-lutidine, 2-methylquinoline, 1-pyrrolidinocyclopentene-2, *n*-isopropylindole, and indole over a 0.5% Pd–1% Ag/Al_2O_3 catalyst. The resulting data presented in Table 2 also show the high efficiency of the bimetallic catalyst, which is comparable to its activity in the hydrogenation of pyridine (Table 1).

CONCLUSIONS

An efficient catalyst was developed for the selective hydrogenation of pyridine and derivatives of it based on bimetallic palladium nanoparticles supported on alumina containing preformed copper or silver nanoparticles on a support.

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