Dedicated to Full Member of the Russian Academy of Sciences A.I. Konovalov on his 85th anniversary

Amino-Modified Silica-Supported Copper–Palladium Alloy. Synthesis and Use in Selective Hydrogenation of Disubstituted Nitroarenes in a Flow Micro Reactor

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Abstract—A copper–palladium catalyst supported on amino-modified silica has been synthesized by chemical reduction. It has been found that submicron particles of a copper–palladium alloy are formed on the silica surface. Unlike commercially available palladium catalysts (Pd/Al₂O₃, Pd/C, Pd/BaSO₄), the synthesized copper–palladium catalyst makes it possible to selectively reduce the nitro group in 3-nitrobenzaldehyde and 1-chloro-4-nitrobenzene.

Keywords: flow chemistry, bimetallic catalysts, selective hydrogenation, copper-palladium alloy.

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INTRODUCTION

Development of catalysts for selective hydrogenation of polyfunctional molecules is a quite challenging and practically important problem; the use of such catalysts could give rise to new synthetic routes to target compounds [1]. Traditionally, palladium is one of the most widely used catalytic metals, and it is successfully utilized to reduce functional groups and remove protecting groups by hydrogenation [2, 3]. However, the catalytic activity of the most common catalyst, Pd/C, is so high that the hydrogenation over Pd/C often leads to exhaustive reduction of all functional groups present in the molecule. This issue is solved by using catalyst poisons [4] or specific supports [5]. In recent time, *d*-metals were added to palladium catalysts to control their activity and selectivity. The bimetallic catalysts thus obtained often showed properties different from the properties of the corresponding monometallic analogs due to electronic modification of palladium atoms as a result of formation of heteronuclear metal-metal bonds [6]. For example, introduction of copper to palladium catalyst made it possible to significantly increase the selectivity

for furfuryl alcohol in the reduction of furfural [7], selectively obtain ethylene by the hydrodechlorination of 1,2-dichloroethane [8], selectively obtain chloroanilines from the corresponding nitro derivatives [9], etc. Furthermore, "dilution" of high-cost palladium with cheap *d*-metals provides a way of reducing the cost of catalyst without substantial loss of catalytic activity and selectivity. Proper estimation of the second metal effect on the catalytic properties of palladium catalysts requires parallel reactions to be carried out under completely identical conditions, which is very difficult to achieve using conventional reactors. In this respect, flow micro reactors offer undoubted advantages; in particular, built-in hydrogen generator and the possibility of accurate temperature, pressure, and flow rate control make them convenient tools for comparative screening of catalytic activity and optimization of reaction conditions, as well as for combinatorial chemistry [10]. In addition, due to effective stirring, fast heat and mass transfer, and reverse pressure control technology which makes it possible to raise boiling point of the solvent, flow micro reactors provide significant increase of the reaction rate [11–13].



Fig. 1. (a) SEM photographs of $CuPd/SiO_2NH_2$ with different magnifications and (b) multilayer EDS map with separate copper and palladium distribution maps.

The present work was aimed at synthesizing copper-palladium catalysts supported on amino-modified amorphous silicon dioxide, studying their morphology, and comparing their activity and selectivity in the catalytic hydrogenation of some difunctional compounds in a flow micro reactor with those of commercially available palladium catalysts.

RESULTS AND DISCUSSION

It is known that one of the key problems of flow chemistry is washout of the active metal [12] with continuous stream of solvent containing reactants, which leads to contamination of the products and shortens the catalyst lifetime. To solve this problem, it was proposed by our research team to use aminomodified silica as a support [14], taking into account that modification of silica surface by donor amino groups provides more efficient metal binding to the support [15]. The same approach was utilized in the present work. The bimetallic copper–palladium catalyst was synthesized by the reduction of a mixture of $CuSO_4 \cdot 5H_2O$ and $Pd(OAc)_2$ with 20 equiv of NaBH₄ in the presence of amino-modified silica in aqueous ethanol. The obtained material (hereinafter $CuPd/SiO_2NH_2$) was analyzed by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS).

The SEM microphotographs of CuPd/SiO₂NH₂ (Fig. 1a, b) show that particles with a size of 100–200 nm are present on the silica surface. These particles form aggregates with different sizes. The multilayer EDS map (Fig. 1c) shows uniform distribution of copper and palladium in the same region, indicating formation of doped bimetallic nanoparticles. The elemental composition of CuPd/SiO₂NH₂ was also determined by EDS; it was found that the catalyst contains copper and palladium atoms in addition to silicon, oxygen, nitrogen, and carbon constituting the amino-modified silica (Fig. 2).

The catalyst structure was also studied by X-ray powder diffraction (Fig. 3). The X-ray powder pattern of CuPd/SiO₂NH₂ showed an intense diffraction peak at $2\theta = 41.76^{\circ}$ located between the corresponding diffraction peaks of Pd (111) ($2\theta = 40.5^{\circ}$) and Cu (111) ($2\theta = 43.2^{\circ}$). This peak can be assigned to the Pd–Cu alloy phase, namely to reflection from the (111) plane of the crystal. According to the JCPDS card no. 48-1551, these data completely conform to face-centered cubic crystals of Pd/Cu alloy (space group *Fm3m*). Apart from the Pd/Cu (111) peak ($2\theta = 41.76^{\circ}$), additional diffraction peaks were observed at $2\theta = 48.35$, 71.16, 86.25, and 91.22° due to reflections from the (200), (220), (311), and (222) planes of Pd/Cu crystal [16].

The degree of oxidation of metals was estimated by X-ray photoelectron spectroscopy (XPS). The XPS spectrum of a sample of CuPd/SiO₂NH₂ in the copper region (Fig. 4a) contained main peaks $2p^{3/2}$ 932.6 eV and $2p^{1/2}$ 952.7 eV, as well as a satellite peak at 942.9 eV. According to published data, Cu^0 gives $2p^{3/2}$ and $2p^{1/2}$ peaks at 933 eV and 953 eV, respectively; $2p^{3/2}$ peak of Cu^I and Cu^{II} appears at 932.5 eV, and the halfwidth of the $2p^{3/2}$ peak is 1.9 eV for Cu^I and 3.4 eV for Cu^{II} [17]. In our case, the $2p^{3/2}$ halfwidth was 3.0 ± 0.1 eV which better matches Cu^{II}. The presence of a satellite peak at 942.9 eV is also typical of Cu(II). However, the intensity of the satellite peak of CuPd/SiO₂NH₂ is not high, whereas the intensity of satellite peaks in samples containing Cu(II) is usually no less than 40% of the $2p^{3/2}$ peak intensity [18]. Thus, the catalyst contains both CuO and Cu₂O, but the presence of Cu(0) cannot be excluded on the basis of the available data since Cu(0) signals are completely overlapped by the signals of copper oxides. Taking into account the ease of oxidation of Cu⁰ and the depth of the XPS analysis which is limited to 5-10 nm, we



Fig. 2. EDS spectrum of CuPd/SiO₂NH₂.



Fig. 3. X-Ray powder pattern of CuPd/SiO₂NH₂.

presume that copper atoms in the alloy are oxidized on the particle surface. The XPS spectrum of CuPd/SiO₂NH₂ in the palladium region (Fig. 4b) showed main peaks at 335.4 and 340.8 eV, which correspond to $3d^{5/2}$ and $3d^{3/2}$ of Pd(0), respectively [19]. The obtained data suggests that the catalyst CuPd/SiO₂NH₂ contains particles of Cu/Pd alloy coated by copper(I) and copper(II) oxides.

The influence of copper on the selectivity and catalytic activity of palladium particles was estimated in the hydrogenation of nitroarenes with molecular hydrogen in a flow reactor. The catalysts were packed in 30-mm steel cartridges which were mounted in a ThalesNano H-Cube Pro[™] flow reactor equipped with a built-in hydrogen generator, an automated sampler, and a six-position switch allowing successive comparative screening of 6 different catalysts. Among commercially available palladium catalysts, we



Fig. 4. X-Ray photoelectron spectra of CuPd/SiO₂NH₂ in the (a) copper and (b) palladium regions.

selected 5% Pd/Al₂O₃ (THS 01118), 5% Pd/BaSO₄ (THS 03112), and 5% Pd/C (THS 02131) manufactured by ThalesNano. The reaction conditions were optimized using 4-nitroaniline as model substrate; the optimal conditions ensured 100% conversion with all catalysts (Table 1). Tetrahydrofuran was used as solvent since it equally well dissolves the initial nitro compounds and hydrogenation products. The progress of the model reaction was monitored by GC/MS.

Having found optimal conditions for the hydrogenation of 4-nitroaniline, we compared the catalytic activities and selectivities of palladium-containing catalysts in the hydrogenation of 3-nitrobenzaldehyde in which both nitro and carbonyl group can be reduced. It was found that the catalyst and support nature directly affect the catalytic activity. The most active was Pd/Al₂O₃ which caused exhaustive reduction of both nitro and carbonyl group and even the aromatic ring (Table 1). The next in activity was Pd/C which reduced the carbonyl group to hydroxymethyl; in addition, a small amount of *m*-toluidine was formed. 3-Aminobenzyl alcohol was selectively formed in the hydrogenation over Pd/BaSO₄, whereas CuPd/SiO₂NH₂ selectively reduced the nitro group while the carbonyl group remained intact. Another substrate tested was 4-nitro-1-chlorobenzene which is capable of undergoing catalytic hydrodehalogenation. The relative activities of the examined catalysts with respect to 4-nitro-1-chlorobenzene were the same as in the hydrogenation of 3-nitrobenzaldehyde. The reduction of the nitro group in the presence of Pd/Al₂O₃ was accompanied by complete hydrodechlorination; mixtures of 4-chloroaniline (major product) and aniline were formed in the hydrogenation catalyzed by Pd/C

and Pd/BaSO₄; and CuPd/SiO₂NH₂ ensured selective reduction of the nitro group without involving the halogen. The lower activity of CuPd/SiO₂NH₂ and hence its higher selectivity are related to the presence of catalytically inactive copper atoms in the alloy. This is consistent with the available published data, according to which mixed palladium alloys with *d*-metals show increased selectivity [8] in the hydrogenation of difunctional aromatic amines.

In summary, a copper–palladium catalyst supported on amino-modified silica has been synthesized by chemical reduction with sodium tetrahydridoborate. Using a combination of SEM, EDS, XPD, and XPS methods, we have shown that the synthesized catalyst contains submicron copper–palladium alloy particles on the amino-modified silica surface. Introduction of catalytically inactive copper atoms into the crystal lattice of palladium considerably changes the catalytic activity and selectivity. Unlike commercially available palladium catalysts, the silica-supported copper–palladium catalyst ensures selective reduction of the nitro group in 3-nitrobenzaldehyde and 1-chloro-4-nitrobenzene in a flow hydrogenation reactor.

EXPERIMENTAL

Solvents of chemically pure and analytical grades were purified according to known procedures [20] before use. Commercially available reagents from Sigma–Aldrich and Alfa Aesar were used. Aminomodified silica was prepared as described in [14].

Samples of the catalyst were analyzed with a Carl Zeiss Merlin auto-emission scanning electron microscope (Germany). To minimize effect on the sample,

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Table 1. Catalytic hydrogenation of some nitroarenes with molecular hydrogen over palladium catalysts in a flow reactor^a

^a Reaction conditions: THF, 100°C, flow rate 0.5 mL min⁻¹, p = 10 bar, substrate concentration 0.05 M.

^b According to the GC/MS data; substrate conversion 100%.

the microphotographs were obtained in the secondary electron mode (primary electron accelerating voltage 5 kV, probe current 300 pA). Elemental analysis was performed with an Oxford Instruments AZtec X-MAX energy-dispersive X-ray spectrometer (United Kingdom) at an accelerating voltage of 20 keV and a focal length of 9.6 mm.

The X-ray powder patterns were obtained at room temperature on a Rigaku MiniFlex 600 diffractometer (Japan) equipped with a D/teX Ultra detector (Cu K_{α} radiation, $\lambda = 1.54056$ Å; 40 kV; 15 mA; 2 θ range 10–80°; scanning with a step of 0.02°; no sample spinning).

The X-ray photoelectron spectra were recorded using a SPECS ultrahigh vacuum analytical chamber equipped with an X-ray source with magnesium and aluminum anodes and a Specs Phoibos 150 hemispherical electron energy analyzer; the residual pressure in the chamber did not exceed 5×10^{-10} mbar. All spectra were processed using CasaXPS package [21]. Background was subtracted by the Shirley method after calibration against the carbon 1*s* line (284.8 eV). Gas chromatographic–mass spectrometric analysis was performed on a Shimadzu GCMS-QP2010 Ultra instrument; HP-5MS capillary column, 30 m, film thickness 0.25 μ m; carrier gas helium (purity 99.995%), flow rate 2 mL/min, split ratio 40; injector temperature 250°C; oven temperature programming from 70 to 140°C at a rate of 10 deg/min, 2 min at 140°C, 140 to 250°C at a rate of 10 deg/min; a.m.u range 35–400.

Synthesis of CuPd/SiO₂NH₂. Amino-modified silica, 0.5 g, was added to a solution of 0.1 g (0.39 mmol) of copper(II) sulfate pentahydrate in 30 mL of deionized water, and a solution of 0.05 g (0.24 mmol) of palladium(II) acetate in 15 mL of ethanol was added. A solution of 0.3 g (7.89 mmol) of sodium tetrahydridoborate in 15 mL of deionized water was then added dropwise with stirring and cooling to the resulting suspension. The mixture was stirred for 3 h at 40°C, and the precipitate was separated by centrifugation, washed in succession with water (3×40 mL) and ethanol (3×40 mL), each time being separated by centrifugation, and dried under

reduced pressure (0.02 mm Hg) for 24 h at 120°C. The catalyst was placed in 30-mm steel cartridges with combined steel reticular and Teflon membranes at the inlet under reduced pressure (5 mm Hg), and steel reticular and Teflon membranes were fastened on the outlet using a CatCart Packer[™] tool.

General procedure for hydrogenation in a flow reactor. A vial with a semipermeable membrane was charged with 10 mL of a solution of a nitro compound with a concentration of 0.05 M (10 mL), and the vial was placed in an automated sample feeder of ThalesNano H-CubeTM. The catalyst cartridges were mounted in the 6-channel CatCart ChangerTM. The solution was passed through the reactor with automated sampling under the following conditions: temperature 100°C, pressure 10 bar, flow rate 0.5 mL/min. After a cycle of catalytic screening, the samples were analyzed by GC/MS.

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CONFLICT OF INTERESTS

The authors declare the absence of conflict of interests.

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