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Grafting of palladium nanoparticles onto mesoporous molecular sieve MCM-41: Heterogeneous catalysts for the formation of an *N*-substituted pyrrol

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Abstract

Palladium nanoparticles, obtained by thermochemical reduction of palladium(II) acetate in propylene carbonate or in tetrahydrofuran with added tetrabutylammonium acetate (Bu_4NOAc), were deposited onto mesoporous molecular sieve MCM-41 (spontaneously or after solvent change) to give novel supported metal catalysts, which were characterized by chemical analysis, powder X-ray diffraction, nitrogen adsorption-desorption isotherms and high-resolution transmission electron microscopy (HR TEM). The materials, together with 10% Pd/C reference were utilized as catalysts in the condensation reaction of 2-aminoethanol with *cis*-butene-1,4-diol to afford *N*-(2-hydroxyethyl)pyrrol. Both supported catalysts showed significantly higher conversions that Pd/C, the one prepared in the presence of Bu_4NOAc being the most active. Catalysts isolated after the reaction and used repeatedly showed lower activity than fresh ones. This apparently reflects partial metal leaching from the solid support and aggregation of the metal particles that were demonstrated by catalytic tests and HR TEM measurements, respectively.

Keywords: Palladium; Nanoparticles; MCM-41; Pyrrol; Catalysis; High-resolution TEM; Powder X-ray diffraction

1. Introduction

Palladium compounds play a key role in the synthetic organic chemistry, mainly owing to their ability to catalyze the formation of synthetically important C–C, C–N, C–O, and C–S bonds [1]. Recently, it was demonstrated that many of these reactions can be performed equally well with fine dispersions of the palladium metal [2]. As compared to their bulk counterparts, metallic nanoparticles offer large surface area, high numbers of corners and edges as well as a high surface tension. Together with the fact that no elaborate ancillary ligands (typically phosphines) are required, this makes them particularly attractive for catalytic utilization [3].

The first mesoporous molecular sieves with narrow pore size distribution were prepared at Mobil Research and Development Corporation in early 1990s [4], by using supramolecular surfactant assemblies (namely long-chain alkyl amines) as the structure-directing agents, which were subsequently removed by calcination or solvent extraction [5]. Materials thus prepared are typically amorphous solids showing ordering on a longer distance. Later, it was demonstrated that variation of the structure-assembling agent allows for obtaining materials with the pore size ranging from about 2 nm up to 30 nm and large surface areas, exceeding even 1000 $m^2\,g^{-1}$ [6].

Mesoporous molecular sieves were extensively utilized in the preparation of reusable, noble-metal catalysts. One of the most commonly employed approaches towards catalyst immobilization is the attachment of a ligand in a noble metal complex onto the sieve surface via covalent bonds [7]. The resulting, so-called hybrid catalysts usually exert higher selectivities than conventional heterogeneous catalysts. In addition, they can be easily separated from the reaction mixture and re-used. Unfortunately, the noble metal leaching from the support, which causes a decrease in the catalytic activity, often complicates recycling of these catalysts.

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A complementary method for the preparation of highly active supported catalysts is represented by impregnation of a support with an appropriate metal precursor that is subsequently transformed into a catalytically active form [6,8], sometimes nanosized metal species [9]. Grafting of pre-formed noble metal nanoparticles onto solid supports has been studied much less [3a]. Palladium nanoparticles can be prepared by electrochemical, photochemical [10] or sonochemical reduction of metal salts [11]. However, the method used most commonly is a simple chemical reduction. It is usually achieved by action of alcohols, sodium tetrahydridoborate or molecular hydrogen in the presence of stabilizing agents that prevent aggregation of the metal particles, which are typically polymers [12], dendrimers [13], surfactants [14] or just highly polar solvents (e.g., propylene carbonate) [15]. The presence of these protecting agents is essential for preserving catalytic activity of the nanoparticles, as the latter dramatically drops with growth (aggregation) of the metal particles.

In this work we report about preparation and characterization of MCM-41-supported, chemically generated palladium nanoparticles and present a comparative catalytic study on their utilization in the palladium-catalyzed reaction of 2-aminoethanol with *cis*-butene-1,4-diol to give *N*-(2-hydroxyethyl)pyrrol [16,17].

2. Results and discussion

2.1. Preparation and characterization of the catalysts

Palladium nanoparticles were prepared by thermochemical reduction of palladium(II) acetate in propylene carbonate which itself served as the particle stabilizing agent [15] (catalyst I) or in tetrahydrofuran in the presence of tetrabutylammonium acetate [14] (catalysts II–IV). The nanoparticle dispersions were then mixed with mesoporous molecular sieve MCM-41, so as to give catalysts with palladium loading 0.1 mmol g^{-1} (catalysts I and II), 0.05 mmol g^{-1} (catalyst III), and 0.2 mmol g^{-1} (catalyst IV). The nanoparticles stabilized with the ammonium salt adsorbed spontaneously onto the molecular sieve immediately after the addition of the molecular sieve. By contrast, an addition of MCM-41 to the nanoparticles generated in propylene carbonate left the metallic particles virtually intact even after stirring for more than 12 h at room temperature. The deposition was finally induced by addition of a less polar solvent (diethyl ether).

The supported catalysts were filtered, thoroughly washed with diethyl ether and dried shortly in the air. We have observed that the final drying has a dramatic effect on the catalytic activity. For instance, catalysts dried at 40 °C overnight exerted significantly lower conversions (about two times), than those dried only at room temperature for 1 h so as to not evaporate all the diethyl ether. Hence, the catalysts presented in this study were worked up by the latter method. We assume that the observed loss of catalytic activity results predominantly from destabilization of the metallic particles after removal of the polar solvate molecules. Increased stability of palladium nanoparticles in polar solvents is well established; however, the exact nature of the stabilization mechanism remains yet unknown [15a].

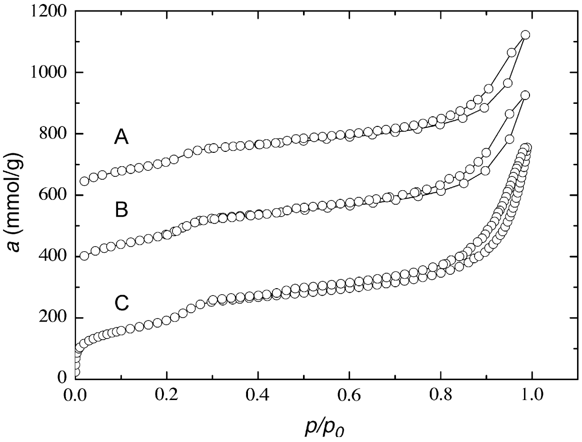

Fig. 1. Nitrogen adsorption isotherms of catalyst I (A), catalyst II (B) and MCM-41 (C). Isotherms for catalysts I and II are shifted by 300 and 550 mmol g^{-1}, respectively.

The supported catalysts were characterized by chemical analysis, powder X-ray diffraction, nitrogen adsorption isotherms and high-resolution transmission electron microscopy. It is noteworthy that the palladium loading calculated from the mass balance corresponded well with that determined by optical emission spectroscopy for mineralized samples, which points to a virtually complete reduction of the palladium precursor and deposition of the formed nanoparticles.

X-ray powder diffraction patterns observed for calcined mesoporous MCM-41 and catalysts I and II are very similar, showing three distinguishable peaks with $2\theta < 10°$ that correspond with the ordered hexagonal framework of the parent MCM-41. This indicates that the structure of MCM-41 remains largely unaffected; a lower diffraction intensity of the Pd-MCM-41 materials as compared with their parent MCM-41 can be ascribed to a lower regularity of the catalysts as compared with the parent sieve.

Nitrogen adsorption isotherms recorded at −196 °C (Fig. 1) show characteristic increase in the adsorbed amount of nitrogen at about 0.3 (p/p_0) due to capillary condensation. Textural parameters, determined from the isotherms, indicate that the adsorption of the palladium nanoparticles causes a decrease in the surface area as well as the pore size (see Table 1).

2.2. Catalytic experiments

Catalytic activity of the newly prepared supported catalysts was assessed in the reaction of *cis*-butene-1,4-diol with

Table 1
Textural properties of MCM-41, catalysts I and II, and commercial 10% Pd/C

	S ($m^2\,g^{-1}$)	V_{meso} ($cm^3\,g^{-1}$)	d_{meso} (nm)
Catalyst I	539	0.169	2.9
Catalyst II	583	0.183	3.1
MCM-41	688	0.919	3.2
10% Pd/C	226	–	–