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Ligand-Assisted Preparation of Palladium Supported Nanoparticles: a Step toward Size Control

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Supported nanoparticles (SNPs) with narrow size distribution were prepared by H_2 reduction of Pd^{2+} previously bound to ligand-modified silica surfaces. Interestingly, the size of the Pd^0 SNPs was tuned by the ligand grafted on the support surface. Amino- and ethylenediamino-functionalized supports formed Pd^0 SNPs of ca. 6 and 1 nm, respectively. The catalytic properties of both Pd^0 SNPs were investigated.

Precise control of the size of metal nanoparticles (NPs) is essential for further application of their unique chemical and physical properties, which are generally size- and shape-dependent.[1] The preparation of soluble metal NPs involves mainly chemical methods, which can result in good control of the particles' shape, size, and size distribution as well as an easy change of the solubility and stability of NPs in solution by ligand exchange and coating.[2,3] The selection of the metal precursor (metal salts or organometallic compounds), reducing agent, protective agent, and solvent will determine the proper conditions for the NPs' nucleation and growth to the desired size and shape. However, the preparation of metal supported NPs (SNPs) following the modern nanocluster approach,[3] which assumes reproducible syntheses, well-defined composition, <10 nm particle size, and narrow size distribution, is not trivial. Examples of the size-controlled synthesis of SNPs include the use of nanoporous materials as templates for the formation of NPs inside the pores.[4] Traditionally, metal supported particles are formed by the reduction of metal precursors previously impregnated onto solids, while the size of the metal nanoparticles formed directly on the support is tentatively controlled by the concentration of the metal and its distribution in the support itself. Nevertheless, the synthesis of SNPs can experience severe problems of aggregation of the metal particles on the external surface of the support. Surfactant-assisted metal reduction can be helpful in locating the nanoparticles inside the pores of the support.[5] Mesoporous solids previously functionalized with suitable anchor units, such as ligands[6] or dendrimers,[7] are also alternatives for efficient immobilization and stabilization of nanoparticles of well-defined size and aggregation. In this Communication, we demonstrated the use of ligand-assisted synthesis of Pd^0 SNPs, where control of the particle size was achieved by varying the ligands grafted on the support surfaces.

The catalyst support consists of silica-coated magnetic NPs (FFSi) prepared following the procedure described recently.[8] The magnetic properties permit a rapid and efficient isolation of the catalyst by application of an external magnetic field. Recovery of catalysts, sampling, and recycling studies are tremendously facilitated because the liquid-phase-containing products (catalyst free) can be withdrawn while keeping the catalyst untouched inside the reactor.

The catalyst was prepared following a few steps. First, the support surfaces were functionalized with different ligands by using organosilane reagents: (3-Aminopropyl)triethoxysilane and [3-[(2-aminoethyl)amino]propyl]trimethoxysilane were used to prepare amino- ($FFSiNH_2$) and ethylenediamino (FFSien)-functionalized solids. The presence of free NH_2 groups on the solid was confirmed and quantified by the

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colorimetric ninhydrin method.[9] As a result, $FFSiNH_2$ and FFSien contain 2.5 and 2.2 mmol of NH_2/g of solid, respectively. Then, the ligand-modified silica supports were submitted to solutions containing Pd^{2+} ions.[10] The final concentration of palladium in both solids, after magnetic separation and washing, is ca. 1.7 wt % or 0.16 mmol of Pd/g of solid. It represents a molar excess of ligands per mole of palladium.

The Pd^{2+}-loaded solids were suspended in cyclohexene (2500 mol/mol of metal) and submitted to H_2 gas at 6 atm (constant) in a Fisher−Porter reactor under stirring and heating (75 °C). The formation of Pd^0 SNPs and the concomitant reduction of cyclohexene, which can serve as the reporter reaction for formation of the active catalyst,[11] were followed by the consumption of H_2 right after the catalyst precursors (supported Pd^{2+}) were submitted to H_2 pressure until total consumption of the substrate (see the Supporting Information). The active catalysts were then magnetically recovered and properly placed in a carbon-coated copper grid to be examined by transmission electron microscopy (TEM). The solid support FFSi is comprised of silica spheres of ~30−50 nm containing magnetic cores (Fe_3O_4 NPs ~ 10 nm) and Pd^0 NPs with the size highly affected by the nature of the ligand (Figure 1a,b). In the amino-modified support surfaces, Pd^0 NPs of 6.4 ± 1.4 nm were formed, and in the ethylenediamino-modified support surfaces, Pd^0 NPs of 1.3 ± 0.3 nm were found, as shown in the size distribution histograms of Figure 1a′,b′. Energy-dispersive spectroscopy (EDS) analysis confirmed the presence of Pd atoms as the main component of the small NPs (Figure 2a) and the presence of Fe atoms in the core NPs (Figure 2b), as displayed in Figure 2.

Considering that all of the conditions used in the preparation of both catalysts, $FFSiNH_2Pd$ and FFSienPd, were exactly the same, except for the ligands grafted on the solid surfaces, one can realize that the monodentate NH_2 ligand assisted the formation of ca. 6 nm Pd^0 NPs and the bidentate ethylenediamino ligand, which also contributes to a chelate effect in the Pd^{2+} complex precursor, assisted the formation of ca. 1 nm Pd^0 NPs. In order to better understand the role of the ligands grafted on the silica support, we examined the possibility of preparing Pd SNPs without any modification on the support surfaces. The nonfunctionalized solid was loaded with Pd^{2+} (1.34 wt % of Pd after magnetic separation and washing),[10] and the metal was reduced by H_2 under conditions similar to those used with the functionalized solids to prepare Pd^0 NPs. The morphology of the catalyst, FFSiPd, and the distribution of the SNPs on the solid were examined by TEM. The sample contains a few isolated Pd^0 NPs of ca. 5 nm and very irregular metal aggregates (Figure 3a). The high-resolution (HR)TEM image (Figure 3b) revealed metal aggregates comprised of multiple particles with an interplanar distance of 0.22 nm, which is in agreement with the (111) lattice spacing of Pd bulk.

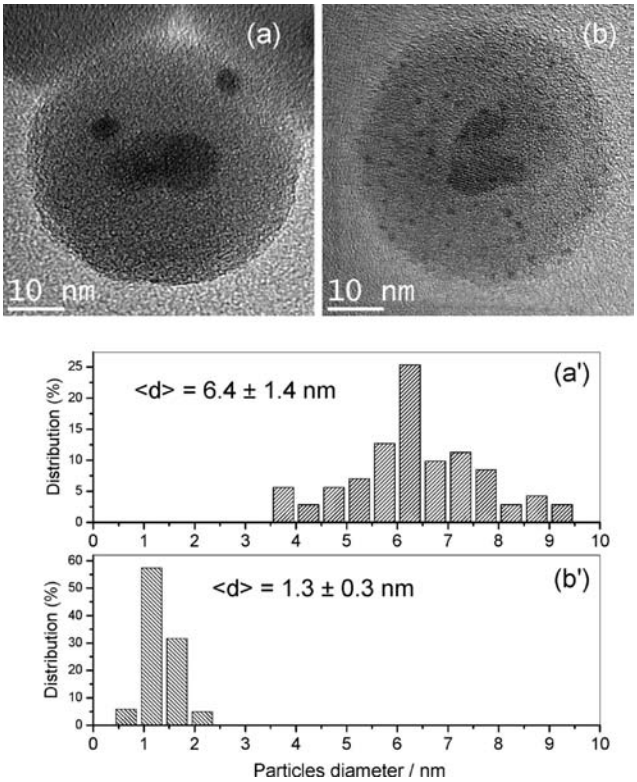

Figure 1. TEM images of the Pd^0 SNPs on (a) amino-modified silica spheres ($FFSiNH_2Pd$) and (b) ethylenediamino-modified silica spheres (FFSienPd). (a′ and b′) Histograms showing the particle size distribution of particles found in enlarged images (see Figure S1 in the Supporting Information).

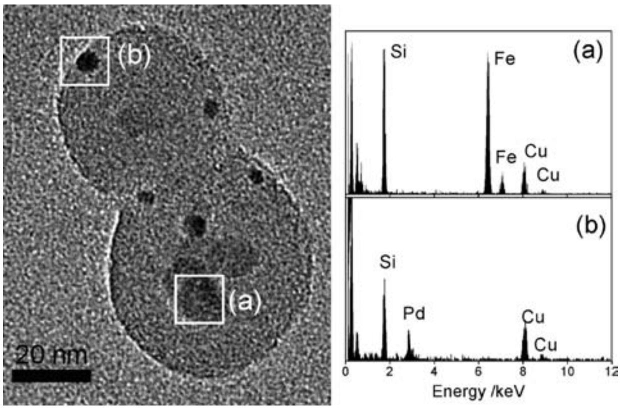

Figure 2. TEM image and EDS analysis of (a) Fe_3O_4 NP present in the core and (b) Pd^0 NP present on the surface of amino-modified silica spheres of $FFSiNH_2Pd$.

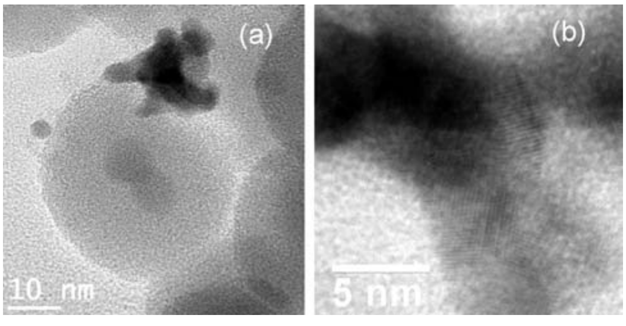

Figure 3. (a) TEM image of the Pd^0 SNPs on nonfunctionalized silica spheres (FFSiPd) and (b) HRTEM image of Pd aggregates.

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(10) In a typical preparation, 100 mg of a silica-coated magnetic support (prepared according to ref 8) was added to 40 mL of a palladium acetate−toluene solution (0.5 mmol/L). The suspension was stirred for 2 h at room temperature. The solid was recovered magnetically, washed with ethanol and acetone, and dried in vacuum. The amount of Pd in the final solids was determined by ICP OES analysis: 1.76 wt % ($FFSiNH_2Pd$), 1.67 wt % (FFSienPd), and 1.34 wt % (FFSiPd).

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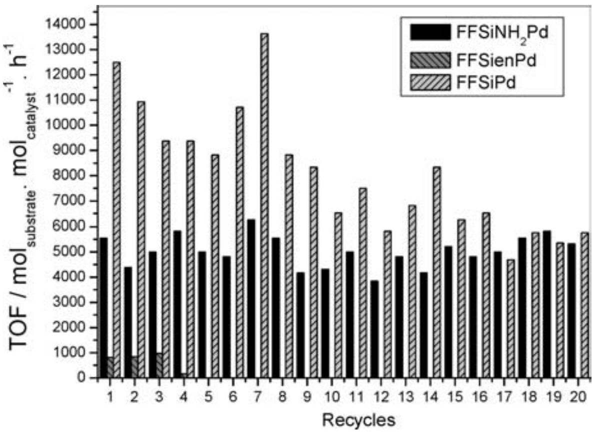

Figure 4. Successive hydrogenations of cyclohexene by supported Pd^0 catalysts. Conditions: 23.5 mmol of cyclohexene, 60 mg of supported catalyst (2500 mol of substrate/mol of catalyst), 75 °C, and 6 atm of H_2.

To rationalize the particle size effect observed, it is reasonable to think that the lability of the metal complex formed by coordination of Pd^{2+} to the ligands/support plays an important role. The bidentate ethylenediamine functional groups should formally coordinate to the Pd^{2+} precursor, thus resulting in nucleation sites for the formation of small monodisperse NPs well-dispersed all over the solid. The monodentate amino group may not strongly coordinate to Pd^{2+} ions, thus allowing diffusion of molecular species and NP growth. In line with that is the behavior of the nonfunctionalized solid because the Pd^{2+} monomers are expected to be only weakly bound to the silanol groups (or physically adsorbed on the support surface), thus allowing diffusion of metal ions, particle growth, and aggregation.

The Pd^0 SNPs prepared in situ catalyzed the hydrogenation of cyclohexene to cyclohexane with quite different reaction rates (see Figure S3 in the Supporting Information). The complete conversion of a fixed amount of substrate, 2500 mol/mol substrate-to-catalyst ratio, lasts ca. 187 min (FFSienPd) and 27 min (FFSiNH$_2$Pd), corresponding to turnover frequencies (TOF) of 800 and 5500 h^{-1}, respectively. Therefore, the catalyst comprised of small Pd^0 nanoparticles (ca. 1 nm) is less active than the catalyst comprised of ca. 6 nm Pd^0 nanoparticles. Interestingly, the catalyst supported on a nonfunctionalized solid, FFSiPd, is more active with a TOF of 12 500 h^{-1} (TOF not corrected for exposed metal), under the same reaction conditions. The effect of the nanocatalyst size on the catalytic activity has been extensively studied in the literature, and decreasing the nanoparticle size does not always result in increased reaction rates.[12,13] Actually, in the nanosize range, size-dependent catalytic activities arise from either electronic or geometric effects, such as the presence of low-coordinated sites, differences in metal-to-ligand bond dissociation energies (BDEs), lattice distortions, different types of facets, the presence of edges, and support interactions, to name a few.[13] In this study, we probably have both size and support effects (different ligands) that may affect the catalytic activity of our catalysts.

Further experiments were performed to verify the stability of the Pd^0 SNPs by recycling the magnetically recoverable catalyst in successive hydrogenation reactions. FFSiPd and FFSiNH$_2$Pd were reused in 20 successive runs of 2500 turnovers each (total turnovers of 50 000), by the addition of new portions of cyclohexene to the magnetically recovered solid. The FFSiNH$_2$Pd catalyst did not show a significant change in the catalytic activity after 20 recycles. FFSiPd is the more active catalyst (FFSiPd > FFSiNH$_2$Pd > FFSienPd), but the catalytic activity decreased as the catalyst was reused in successive reactions. FFSienPd is the less active catalyst and deactivated completely after the fourth recycle (Figure 4).

The FFSienPd catalyst deactivation is probably not related to the loss of metal because negligible amounts of metal were found in the organic products collected from the reuse experiments [$<$ 0.01 ppm Pd by inductively coupled plasma optical emission spectroscopy (ICP OES) analysis]. Interestingly, metal leaching was also negligible after the 20th reuse of the FFSiPd catalyst ($<$ 0.06 ppm Pd in the products), but the FFSiNH$_2$Pd catalyst lost 0.25 wt % of the initial Pd content to the organic phase after 20 recycles. We performed new catalytic hydrogenation experiments using the postcatalysis solutions, obtained after removal of the catalyst magnetically, and a new portion of the substrate. Under our standard experimental conditions, no catalytic activity was observed for the postcatalysis solutions isolated from both FFSiNH$_2$Pd and FFSiPd catalysts. This excludes the presence of any leached molecular species responsible for any catalytic activity in the recovered solution, while the isolated magnetically recovered solids are still catalytically active (see Figure S4 in the Supporting Information). The high stabilization of the Pd^0 NPs on the magnetic support surfaces can explain the high reusability of the FFSiNH$_2$Pd catalyst without noticeable metal loss or particle aggregation during the catalytic cycles but cannot explain the deactivation of the FFSienPd catalyst, which probably is related to metal–support interactions or metal poisoning, which is in agreement with the stronger nanocluster-to-ligand BDEs expected in smaller particles.[12a]

In summary, we have tuned the size of metal SNPs by changing the functional groups present on the solid support surfaces. The metal-complex precursors formed by the coordination of Pd^{2+} to the ligands grafted on the silica surfaces apparently permit the stabilization of Pd^0 NPs of different sizes and well-dispersed on the support surface. We suggested here a ligand-assisted approach for the preparation of metal SNPs, which represents a step toward size control of SNPs. Additional experiments and control arrangements are in progress in order to elucidate the mechanism of SNP formation.

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Supporting Information Available: Experimental details, hydrogenation curves, and TEM images. This material is available free of charge via the Internet at http://pubs.acs.org.

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