CHEMISTRY OF MATERIALS

VOLUME 18, NUMBER 10 MAY 16, 2006

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# Communications

## Synthesis and Applications of Magnetic Nanocomposite Catalysts

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*Received December 30, 2005*
*Revised Manuscript Received March 21, 2006*

Polymer- or $SiO_2$-coated magnetic nanoparticles have been widely investigated due to their superparamagnetic properties and biocompatibility.[1–4] For many applications, these magnetic nanoparticles would benefit from having $SiO_2$ or polymer shells to impart ease of functionalization and biocompatibility. Poly(ethylene glycol) conjugation onto the $SiO_2$ layer has increased cell uptake efficiency in silica-coated magnetic nanoparticles and made them feasible for cell separation applications.[1] Self-assembled block copolypeptides on magnetic nanoparticles could be used as a smart drug delivery system controlled by magnetic field.[2] Magnetic nanoparticles can also be processed with quantum dots within a silica matrix to yield magnetic and fluorescent nanocomposites.[3] Layer-by-layer synthesis,[5] charged particle interaction,[6] and mercaptosilane functionalization[7] have been proposed to form various architectures of transition metal nanoclusters with silica nanospheres. These strategies can be employed to derive a novel heterogeneous catalyst system, whereby the high surface-to-volume ratio of transition metal nanoclusters can be used to achieve high reactivity. However, such ultrafine particles do not facilitate large-scale separations by conventional methods in liquid-phase processes. To allow for the easy removal of catalysts from reaction mixtures, supports containing magnetic nanoparticles have been developed.[8–11] However, silica-coated magnetic nanoparticles have not been studied as a catalyst support.

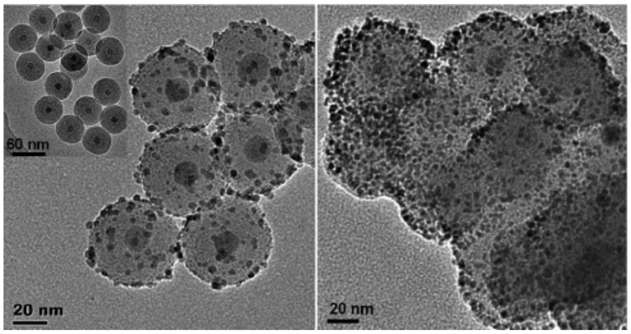

**Figure 1.** TEM micrographs of as-prepared $SiO_2/Fe_2O_3$ (left inset), Pd/HS-$SiO_2/Fe_2O_3$ (left), and Pd/$H_2N$-$SiO_2/Fe_2O_3$ (right).

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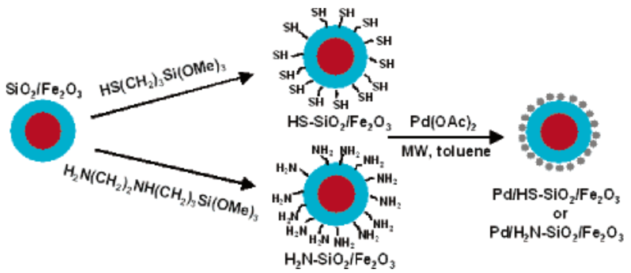
10.1021/cm052885p CCC: $33.50 © 2006 American Chemical Society
Published on Web 04/20/2006

**Scheme 1. Synthesis of Pd/$SiO_2$/$Fe_2O_3$ Nanocomposites**



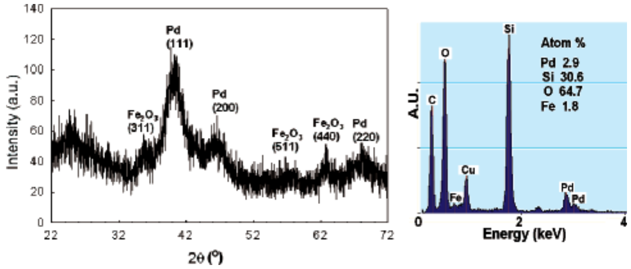


**Figure 2.** XRD pattern (left) and EDX spectrum (right) of Pd/$SiO_2$/$Fe_2O_3$ nanocomposites.

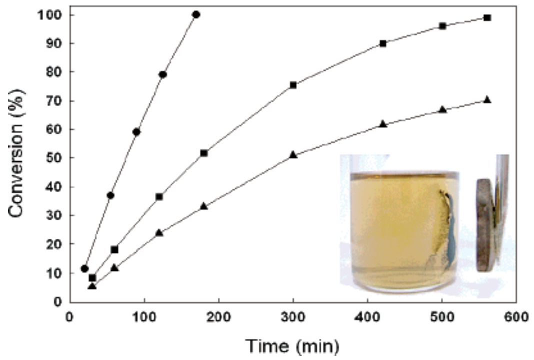


**Figure 3.** Conversion of hydrogenation of nitrobenzene over (●) Pd/$H_2N$-$SiO_2$/$Fe_2O_3$, (■) Pd/HS-$SiO_2$/$Fe_2O_3$, and (▲) commercial Pd/C. (Inset) Magnetic separation of Pd/$H_2N$-$SiO_2$/$Fe_2O_3$ from the reaction medium.

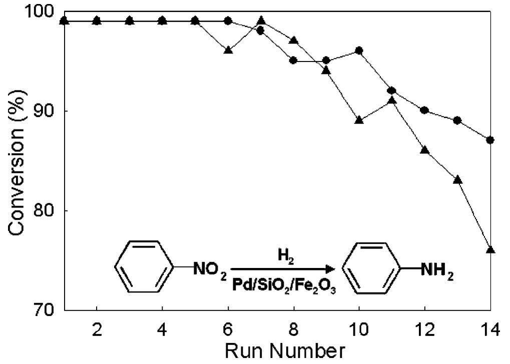


**Figure 4.** Hydrogenation of nitrobenzene over (●) 2.5 mg of Pd/$H_2N$-$SiO_2$/$Fe_2O_3$ and (▲) 2.2 mg of Pd/HS-$SiO_2$/$Fe_2O_3$ over multiple runs. In both cases, 2 mmol of nitrobenzene was reacted in 6.5 mL of 2-propanol with 2 $\mu$mol of Pd catalyst at room temperature and 1 atm of $H_2$. Conversion for each run was measured by gas chromatography (GC) after 90 and 290 min for Pd/$H_2N$-$SiO_2$/$Fe_2O_3$ and Pd/HS-$SiO_2$/$Fe_2O_3$, respectively.

In this communication, we report on the synthesis of a nanocomposite of Pd nanoclusters supported on silica-coated $Fe_2O_3$ nanoparticles (Scheme 1). This Pd/$SiO_2$/$Fe_2O_3$ catalyst system was successfully applied to hydrogenation reaction. First, monodisperse silica-coated $Fe_2O_3$ nanoparticles ($SiO_2$/$Fe_2O_3$) were derived in water-in-cyclohexane reverse microemulsion.[3,12] They were functionalized with mercapto and amine functionalities, which have been known to have strong affinity with transition metal nanoclusters, such as Pd,[7] $Fe_3O_4$,[13] and Au.[14] In this study, 225 mg of $SiO_2$/$Fe_2O_3$ was functionalized with 0.045 mmol of (3-mercaptopropyl)-trimethoxysilane (MPS) and *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AAPS) by refluxing in toluene for 30 h.[7] Next, Pd was introduced as $Pd(OAc)_2$ to the surface functionalized $SiO_2$/$Fe_2O_3$ in toluene under microwave (300 W, 15 min). The resulting black colloidal particles were collected by a magnet, washed with toluene three times, and dried in vacuo. Transmission electron microscopy (TEM) images show that Pd nanoclusters were deposited onto the $SiO_2$/$Fe_2O_3$ nanoparticles with ~20 nm thick $SiO_2$ shell (see Figure 1). The size and distribution of Pd nanoclusters on the $SiO_2$/$Fe_2O_3$ support were dependent on the affinity ligands used. When AAPS was employed, smaller Pd nanoclusters ($2.2 \pm 0.7$ nm) and narrower cluster size distribution were obtained from a random selection of 300 Pd/$SiO_2$/$Fe_2O_3$ nanocomposites in TEM micrographs. MPS gave rise to Pd clusters of $2.9 \pm 1.7$ nm. When no affinity ligands were used, $Pd(OAc)_2$ produced isolated Pd nanoclusters that were not properly dispersed on the surface of $SiO_2$/$Fe_2O_3$ (see Supporting Information).

Pd/$SiO_2$/$Fe_2O_3$ nanocomposite showed X-ray diffraction (XRD) peaks corresponding to Pd(0)[15] and $\gamma$-$Fe_2O_3$,[16] and a broad band ($2\theta = 22-30°$) associated with amorphous silica (Figure 2). TEM energy-dispersive X-ray (EDX) spectra confirmed the presence of Pd, Si, O, and Fe (Figure 2). ICP-MS elemental analyses showed that the Pd/HS-$SiO_2$/$Fe_2O_3$ and Pd/$H_2N$-$SiO_2$/$Fe_2O_3$ nanocomposites contained 9.47 wt % and 8.14 wt % Pd, respectively.

Pd/$SiO_2$/$Fe_2O_3$ was examined as a catalyst for the hydrogenation of nitrobenzene. For the kinetics studies, conversion was measured as a function of reaction time, with the turnover number set at 2000 for 100% conversion (Figure 3). Pd/$H_2N$-$SiO_2$/$Fe_2O_3$ showed the highest conversion rate of 0.39 $\mu$mol/s for this hydrogenation reaction. Pd/HS-$SiO_2$/$Fe_2O_3$ and commercial Pd/C (Aldrich) gave conversion rates of 0.12 and 0.08 $\mu$mol/s, respectively.

The magnetic nanocomposite catalysts were easily collected by a magnet for reuse (see Figure 3 inset). Figure 4 shows that Pd/$H_2N$-$SiO_2$/$Fe_2O_3$ and Pd/HS-$SiO_2$/$Fe_2O_3$ gave 99% yield over 6 and 5 consecutive runs, respectively. Their conversions then decreased gradually in subsequent runs to 87% and 76% at run 14. The turnover number was set at 1000 for 100% conversion in each run in Figure 4. ICP-MS

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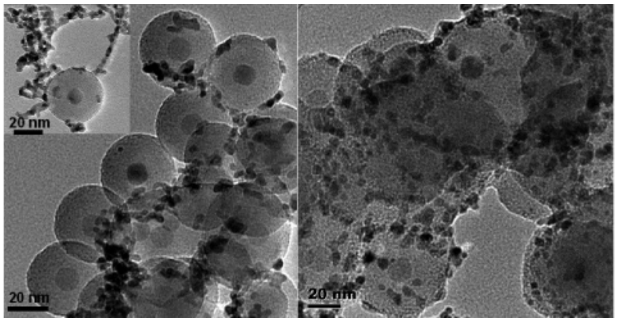

**Figure 5.** TEM micrographs of Pd/HS-$SiO_2$/$Fe_2O_3$ (left) and Pd/$H_2N$-$SiO_2$/$Fe_2O_3$ (right) after 14 runs of nitrobenzene hydrogenation. The left inset shows that Pd nanoclusters became interconnected, and some of the Pd nanoclusters became detached from the HS-$SiO_2$/$Fe_2O_3$ support.

results showed that Pd leaching was negligible.[17] TEM micrographs revealed some grain growth in the Pd nanoclusters in both Pd/$H_2N$-$SiO_2$/$Fe_2O_3$ and Pd/HS-$SiO_2$/$Fe_2O_3$ catalysts after 14 runs (Figure 5). This could have led to the reduced conversions after multiple catalyst recycling. It was also shown that the Pd clusters became agglomerated and interconnected for Pd/HS-$SiO_2$/$Fe_2O_3$ after 14 runs, whereas the Pd nanoclusters remained highly dispersed on $H_2N$-$SiO_2$/$Fe_2O_3$ with an average size of $4.8 \pm 0.9$ nm. The dependency of catalytic reactivity on Pd cluster size and shape has been studied before.[18] In our case, the AAPS might have served as a stronger affinity ligand than MPS to provide for higher Pd dispersion and to more effectively suppress the agglomeration, aggregation, and growth of Pd nanoclusters during the hydrogenation of nitrobenzene. This allowed the Pd/$H_2N$-$SiO_2$/$Fe_2O_3$ catalyst to achieve high conversions within a short reaction time of 90 min (compared to 290 min for Pd/HS-$SiO_2$/$Fe_2O_3$) in each run and to preserve an excellent reactivity even for run 14 (87% conversion).

In summary, we have demonstrated the use of $SiO_2$/$Fe_2O_3$ nanocomposite as a magnetic catalyst support. The silica coating could be easily modified with affinity ligands. Pd nanoclusters were shown to be deposited with high dispersion and stability, especially when AAPS was used as the affinity ligand. The Pd/$SiO_2$/$Fe_2O_3$ nanocomposite catalyst allowed for ease of recycling via magnetic separation. In particular, the Pd/$H_2N$-$SiO_2$/$Fe_2O_3$ catalyst provided excellent reactivity and reusability in the hydrogenation of nitrobenzene.

**Acknowledgment.** This work was funded by the Institute of Bioengineering and Nanotechnology (Agency for Science, Technology and Research, Singapore).

**Supporting Information Available:** XRD pattern of $SiO_2$/$Fe_2O_3$ nanocomposite, TEM micrograph of Pd/$SiO_2$/$Fe_2O_3$ prepared without any affinity ligands, and detailed experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Pd leaching in the 14 runs was 1.2% and 1.4% of the original Pd content for Pd/$H_2N$-$SiO_2$/$Fe_2O_3$ and Pd/HS-$SiO_2$/$Fe_2O_3$, respectively.

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