

## Notes

### Magnetically Recoverable Palladium Nanocatalyst for Chemoselective Olefin Hydrogenation

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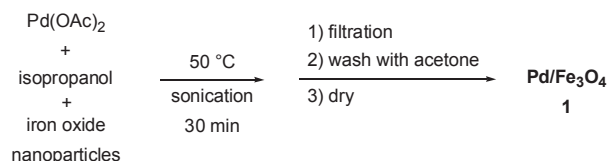
The use of metal nanoparticles as the catalysts has been attracting great attention as a useful strategy for improving the catalytic efficiency of heterogeneous catalysts in a wide range of synthetic transformations.<sup>1</sup> Metal nanoparticles proved to be significantly more efficient than their bulk counterparts due to their large surface area. Recently, we reported the use of palladium nanoparticles entrapped in AlO(OH) matrix as the efficient racemization catalyst in the dynamic kinetic resolution of primary amines.<sup>2</sup> Subsequently, we became interested in the development of more readily recoverable palladium nanocatalyst for practical applications. Naturally, we chose magnetic nanoparticles (MNPs) as the support for the immobilization of palladium nanocatalysts since they can be readily separated from reaction medium by applying an external magnetic field. In most of the previous studies, nanocatalysts including palladium nanocatalyst were immobilized on the modified surface of MNPs.<sup>3-5</sup> The surface modifications of MNPs however are time-consuming and often require non-green reagents. An alternative approach to overcome the limitations would be the direct immobilization of nanocatalysts on the unmodified surface of MNPs without using any harmful reagents. We thus prepared palladium nanocatalysts adsorbed on the unmodified surface of iron oxide MNPs and then tested them as the catalysts for the olefin hydrogenation at room temperature.<sup>6</sup> We herein wish to report the results from these studies.

The chemoselectivity toward two or more reducible functional groups in the catalytic hydrogenation is of great importance. Generally, the chemoselectivity is achieved by poisoning catalysts with ligands such as sulfur or nitrogen-containing molecules.<sup>7</sup> However, this approach suffers from a disadvantage that a large amount of catalysts should be used to compensate their reduced activities. In this work, Pd nanocatalysts adsorbed on iron oxide MNPs (Pd/Fe<sub>3</sub>O<sub>4</sub>, **1**) were prepared in the absence of those ligands but displayed good selectivity in addition to high activity. We observed that a catalytic amount (0.3 mol %) of **1** was enough for high selectivity in most of the tested reactions.

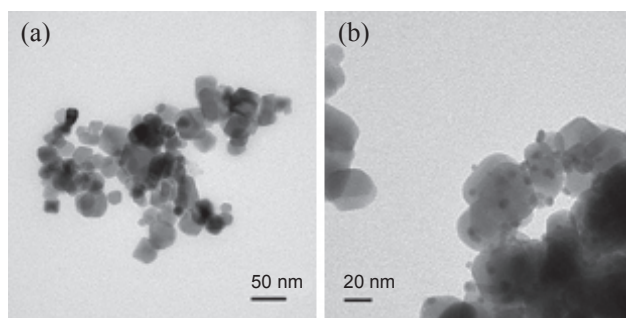
The direct immobilization of Pd on unmodified MNPs was achieved by reducing Pd(OAc)<sub>2</sub> in the presence of iron oxide MNPs (< 50 nm). We used isopropanol (IPA) as both reduc-

tant and solvent. The reaction was carried out with sonication at 50 °C for 30 min. After the reaction was complete, the reaction mixture was filtered, washed with acetone, and then dried under reduced pressure to afford **1** as black powder (Scheme 1). The isolated solid contained 0.45 wt % of Pd, which was determined by Inductively Coupled Plasma (ICP) analysis. Transmission electron microscopy (TEM) analysis showed that spherical shaped Pd nanocatalysts (2 - 3 nm) were directly attached on iron oxide MNPs (30 - 50 nm) (Figure 1).

The hydrogenations of a variety of olefins (0.3 mmol) in the presence of **1** (0.3 mol %) were carried out under 1 atm of H<sub>2</sub> at room temperature. The results are described in Table 1. The catalytic performance of **1** was good in both polar and nonpolar solvents although faster reactions were observed in polar solvents (compare entries 1-3). The hydrogenations of mono- and di-substituted alkenes were complete within 1 hour to provide quantitative yields (> 97%) (entries 1-7). However, the hydrogenation of sterically more hindered tri-substituted alkene such

























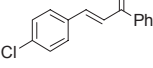
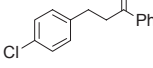


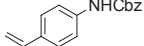
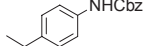


**Scheme 1.** Procedure for the preparation of palladium catalyst



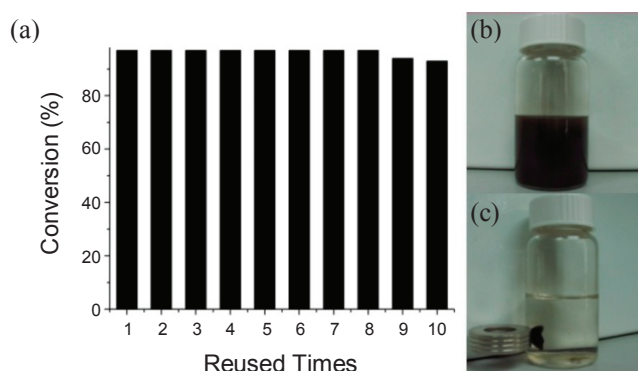
**Figure 1.** TEM images of iron oxide NPs (a) and spherical shaped Pd NPs (2 - 3 nm) directly attached on iron oxide NPs (b).

**Table 1.** Hydrogenation of olefins

entry	solvent	substrate	product	time (h)	yield (%) <sup>b</sup>
1	Toluene			1	> 97
2	THF			0.5	> 97
3	Methanol			0.5	> 97
4	Methanol			0.5	> 97
5	Methanol			0.5	> 97
6	Methanol			1	> 97
7	Methanol			1	> 97
8	Methanol			12	51
9	Methanol			0.5	> 97
10	Toluene			1	> 97
11	Toluene			5	94 <sup>c</sup>
12	Toluene			3	> 97
13	Toluene			1	> 97 <sup>d</sup>
14	Methanol			0.5	> 97 <sup>e</sup>
15	Methanol			0.5	> 97 <sup>e</sup>

<sup>a</sup>Hydrogenation reactions were performed with solutions containing substrate (0.3 mmol) and **1** (0.3 mol %) in 1 mL of solvent at room temperature under an atmospheric pressure of H<sub>2</sub>. <sup>b</sup>The yields were determined by <sup>1</sup>H NMR analysis. <sup>c</sup>As a minor product, 3-phenyl-1-propanol was produced in 6% yield. <sup>d</sup>Dehalogenated product was not produced during 24 h. <sup>e</sup>Hydrogenolized product was not produced during 24 h.

as 1-methylcyclohexene afforded a low yield (51%) even after 12 h (entry 8). A remarkable chemoselectivity was observed in the hydrogenation of difunctional alkenes containing a carbonyl group. In the hydrogenation of cyclic (entry 9) and aromatic  $\alpha,\beta$ -unsaturated ketones (entries 10 and 12), the double bond was selectively hydrogenated without reducing the carbonyl moiety. However, in case of  $\alpha,\beta$ -unsaturated aldehyde such as *trans*-cinnamaldehyde, the partial reduction of carbonyl functionality took place to give a small amount of 3-phenyl-1-propanol (6%)



**Figure 2.** (a) Recycling of Pd nanocatalysts. (b) Pd nanocatalysts dispersed in methanol solution. (c) Pd nanocatalysts recovered with an external magnet.

with 3-phenylpropanal (94%) as the major product (entry 11). Another notable chemoselectivity was observed in the hydrogenation of aromatic halide containing  $\alpha,\beta$ -unsaturated ketone moiety (entry 13). In this case, no dehalogenated products were produced even after 24 h. A useful chemoselectivity was also observed in the hydrogenation of alkenes carrying a protected carboxy or amino functionality (entries 14 and 15). In these cases, the benzyl group in the protecting groups remained intact during the hydrogenation of double bond.

Finally, we explored the recyclability of Pd nanocatalysts in the hydrogenation of *trans*-stilbene. We run the reaction ten times with the recycling of nanocatalysts and observed no substantial loss in activity up to the 8th run (Figure 2a). The catalyst particles were well dispersed in solvent during the reaction but easily recovered on the reaction vessel wall by applying a permanent magnet when the reaction was complete (Figures 2b and 2c). The ICP analysis indicated that the hydrogenated products contained no detectable palladium and therefore Pd leaching was negligible during the recycle reactions.

In summary, we have demonstrated that Pd nanocatalysts directly immobilized on unmodified iron oxide MNPs are active, chemoselective, and readily recyclable in the hydrogenation of olefins. The procedure for immobilizing Pd nanocatalysts is simple and straightforward. Overall, the olefin hydrogenation using Pd nanocatalysts provides a useful tool for organic synthesis.

## Experimental Section

**Synthesis of palladium nanocatalyst adsorbed on unmodified MNPs.** Palladium acetate (8.5 mg, 38  $\mu$ mol) and iron oxide MNPs (796 mg, < 50 nm) were dissolved in isopropanol (20 mL) and sonicated for 0.5 h at 50 °C. The resulting black solution was filtrated by membrane filter (0.2  $\mu$ m pore size) and washed with 2  $\times$  100 mL acetone. After filtration, the catalyst was dried in vacuo to afford the black powder (775 mg, 97% yield). Palladium content on MNPs was determined by Induced Coupled Plasma (ICP) analysis, indicating that 0.45 wt % of Pd was loaded.

**General procedure of catalytic hydrogenation.** Palladium nanocatalyst on MNPs (21.3 mg, 0.3 mol % Pd) was added to

a Schlenk flask and vacuum-dried for 0.5 h at room temperature. Substrate (0.3 mmol) and 1 mL of solvent was added under argon atmosphere. The reaction mixture was stirred at room temperature under H<sub>2</sub> balloon. After the reaction, a small portion of the reaction mixture was collected for NMR analysis.

**Recycle experiment of *trans*-stilbene hydrogenation.** Palladium nanocatalyst on MNPs (21.3 mg, 0.3 mol % Pd) and *trans*-stilbene (54 mg, 0.3 mmol) were added in 1 mL of methanol and stirred at room temperature for 1 h under H<sub>2</sub> balloon. After the reaction was complete, palladium nanocatalyst was recovered on the reaction vessel wall by applying an external magnet and the reaction solution was removed. The recovered nanocatalyst was washed with 2 × 10 mL methanol and then reused for next reaction without any additional treatment. The reaction solutions separated from Pd nanocatalyst were analyzed by <sup>1</sup>H-NMR to determine the conversion % and evaporated under reduced pressure to give solid products. The ICP analysis indicated that the products contained no detectable palladium.

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