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Magnetically Separable Pd Catalyst for Highly Selective Epoxide Hydrogenolysis under Mild Conditions

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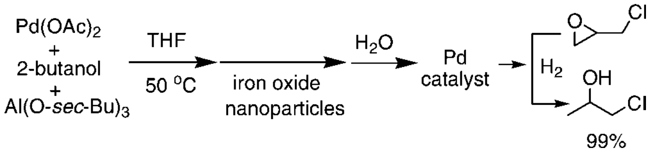
ABSTRACT



A magnetically separable palladium catalyst was synthesized simply through a sol–gel process incorporating palladium nanoparticles and superparamagnetic iron oxide nanoparticles in aluminum oxyhydroxide matrix, which is highly active and selective for epoxide hydrogenolysis at room temperature under 1 atm H_2. The catalyst was recycled for 25 times without loss of the activity.

Metal nanoparticles are extensively used in many organic transformations because of their inherent large surface-to-volume ratio and distinct catalytic activities.[1] Although various metal nanoparticles have been developed in many reactions, they often suffer from particle agglomeration during the reaction as well as from difficulties in separation of the catalyst from the reaction mixtures. To overcome these problems, nanoparticles have been immobilized onto many different supports such as inorganic materials, organic polymers, dendrimers, and ionic liquids.[2] Recently, superparamagnetic nanoparticles have been employed to facilitate catalyst separation by using external magnets.[3] However, the supported catalysts generally have low reactivities, metal-leaching problems, and difficult synthetic procedures.

Herein, we describe a simple synthetic procedure for the preparation of the magnetically separable palladium catalyst that shows high activity in the highly regioselective hydrogenolysis of epoxides at room temperature under 1 atm H_2. The recyclability of the catalyst is remarkable; it retains the original catalytic activity even after recycling 25 times.

Recently, we have developed a simple but new method for preparing recyclable palladium catalysts through generating palladium nanoparticles from $Pd(PPh_3)_4$ under aerobic conditions.[4] With this method, the palladium content of the resulting catalyst was limited up to about 3 wt % because of the solubility of $Pd(PPh_3)_4$ in the reaction mixture. Then,

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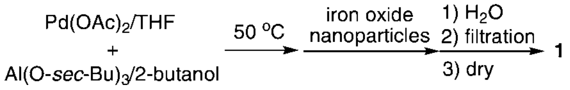
we optimized conditions for substituting palladium acetate for $Pd(PPh_3)_4$, and the palladium content could be increased up to 10 wt % without losing activity per mol of Pd. Furthermore, superparamagnetic iron oxide nanoparticles were able to be readily mixed with the suspension of palladium nanoparticles before gelation. Palladium nanoparticles were produced from a solution of palladium acetate, Al(O-*sec*-Bu)$_3$, 2-butanol, and THF. Iron oxide nanoparticles dispersed in ethanol were added to the resulting black suspension.[5] Then, water was added to form black gel. The gel was isolated by filtration, washed with acetone, and dried at 120 °C for 5 h to give **1** as dark brown powder (Scheme 1).

Scheme 1. Preparation of Catalyst



The catalyst **1** was characterized by transmission electron microscopy (TEM). In the TEM images, iron oxide nanoparticles of 60∼90 nm in diameter and palladium nanoparticles of 2∼3 nm entrapped in fibrous aluminum oxyhydroxide are observed (Figure 1).[6] The specific surface area of **1** was determined to be 579 $m^2 g^{-1}$ by the N_2 BET method at 77 K. The magnetic property of **1** was studied by using a superconducting quantum interference device (SQUID). No hysteresis was observed at room temperature in the magnetization curve, which is a typical superparamagnetic behavior.[7] The saturation magnetization value at room temperature is 4.7 emu g^{-1}, which is sufficient for magnetic separation.

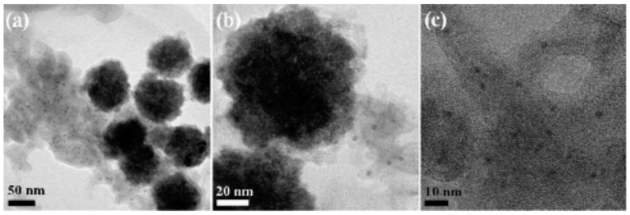
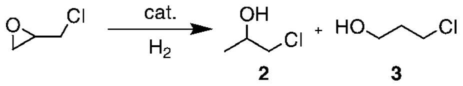


Figure 1. TEM images of **1**: (a) iron oxide nanoparticles (60∼90 nm) and Pd nanoparticles (2∼3 nm) entrapped in AlO(OH); (b) iron oxide nanoparticle, (c) Pd nanoparticles.

We tested the catalytic activity of **1** in epoxide hydrogenolysis to give alcohols.[8] This reductive cleavage reaction has traditionally been carried out by using stoichiometric metal hydrides, in which the problem of waste salts is unavoidable.[9] Therefore, much attention has been paid to the catalytic hydrogenolysis of epoxides with molecular hydrogen or ammonium formate.[10] However, the previous catalyst systems are not suitable to industrial applications because of low yield, low selectivity, low catalyst durability, and/or harsh and complex reaction conditions. For example, the reaction with [Cp*RuCl(cod)] requires the addition of an amine ligand and a strong base under 10 atm of hydrogen pressure.[10d] The use of Pd/C-ethylenediamine complex shows a good selectivity for terminal epoxides, but it suffers from solvolysis and requires 5 atm H_2.[10e] Recently, Yu and coworkers reported that the polyurea-microencapsulated palladium catalyst (PdEnCat) is a recyclable catalyst in epoxide hydrogenolysis, which needs 40 atm H_2 for aliphatic epoxides.[11] Herein, we report a highly efficient and selective epoxide hydrogenolysis under 1 atm H_2 at room temperature by using **1**.

Table 1. Catalytic Activity Comparison[a]



entry	catalyst	time (h)	conversion (%)[b]	product yield (%)[b] **2**	product yield (%)[b] **3**
1	**1**	4	>99	99.8	0.2
2	iron oxide[c]	20	0	0	0
3	AlO(OH)[d]	20	0	0	0
4	5% Pd/C[e]	4	89	83	6
		(20)	(>99)	(91)	(9)
5	5% Pd/Al_2O_3[e]	4	70.9	70	0.9
		(20)	(>99)	(98.3)	(1.7)
6	5% Pd/$CaCO_3$[e]	4	65.1	64.5	0.6
		(20)	(91.3)	(89.1)	(2.2)
7	5% Pd/$BaCO_3$[e]	4	14.9	14.5	0.4
		(20)	(70)	(68.7)	(1.3)
8	4.3% PdEnCat[e]	20	0	0	0

[a] The reaction was performed on 1.0 mmol of epichlorohydrin dissolved in 2.0 mL of EtOAc with 2.0 mol % Pd at 23 °C under hydrogen balloon. [b] Determined by GC. [c] Reaction run using 20 mg. [d] Reaction run using 50 mg. [e] Commercial catalysts.

The catalytic activity of **1** was compared with the activities of various palladium catalysts in the hydrogenolysis of

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(4) (a) Kim, N.; Kwon, M. S.; Park, C. M.; Park, J. *Tetrahedron Lett.* **2004**, *45*, 7057. (b) Kwon, M. S.; Kim, N.; Park, C. M.; Lee, J. S.; Kang, K. Y.; Park, J. *Org. Lett.* **2005**, *7*, 1077. (c) Kwon, M. S.; Kim, N.; Seo, S. H.; Park, I. S.; Cheedrala, R. K.; Park, J. *Angew. Chem., Int. Ed.* **2005**, *44*, 6913. (d) Kim, M.-J.; Kim, W.-H.; Han, K.; Choi, Y. K.; Park, J. *Org. Lett.* **2007**, *9*, 1157.

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(7) See Supporting Information for the characterization of **1**.

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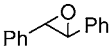
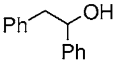
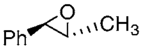
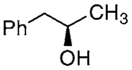
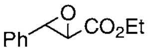
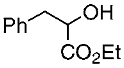
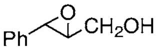
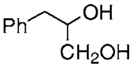
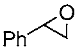
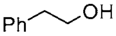
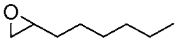
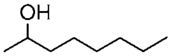
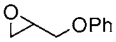
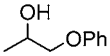
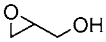
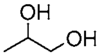
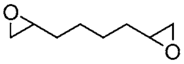
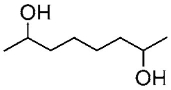
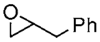
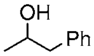
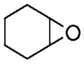
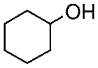
Table 2. Hydogenolysis of Epoxides[a]

entry	substrate	product	time (h)	yield (%)[b]
1			0.5	>99 (94[c])
2			0.7	>99
3			1.0	>99 (95[c])
4			2.0	>99 (94[c])
5			1.5	96
6[d]			8.0	89[e]
7[d]			0.5	>99 (97[c])
8[d]			5.0	>99
9[d]			4.0	85[f]
10[d]			4.0	85[g]
11[d]			20	93

[a] The reaction was performed on 1.0 mmol of substrate dissolved in 2.0 mL of EtOAc with 1.0 mol % Pd at 23 °C under hydrogen balloon. [b] Determined by GC. [c] Isolated yield. [d] Reaction run using 2.0 mol % of Pd. [e] 1-Octanol was produced in 4% yield. [f] 1,8-Octanediol was produced in 8% yield. [g] 3-Phenyl-1-propanol was produced in 15% yield.

epichlorohydrin (Table 1). AlO(OH) or iron oxide itself did not show any activity for the hydrogenolysis. The catalyst **1** showed better activity and selectivity than all of the commercial catalysts such as Pd/C, Pd/Al$_2$O$_3$, Pd/CaCO$_3$, Pd/BaCO$_3$, and PdEnCat. In the cases of Pd/C and Pd/Al$_2$O$_3$, 5 times longer reaction time is required to complete the reaction and 3-chloro-1-propanol was produced as a byproduct in 9% and 2% yield, respectively. In the cases of Pd/CaCO$_3$ and Pd/BaCO$_3$, even after 20 h, the reactions were not completed. Particularly, PdEnCat did not show any activity at room temperature under 1 atm H$_2$.

It is notable that **1** can be reused at least 25 times without activity loss through a simple recovery by an external magnet. The yields of 1-chloro-2-propanol in the 1st−21st use were measured by GC after 90 min; they were consistently about 65%. Increasing the reaction time to 4 h in the 22nd−25th use increased the yield to more than 94% yield.[12]

The hydrogenolysis with **1** was applicable for a wide range of epoxides (Table 2). The bond between the benzylic carbon and oxygen was cleaved almost exclusively in the hydrogenolysis of benzylic epoxides (entries 1−5). Notably, *trans*-stilbene oxide was transformed exclusively into 1,2-diphenylethanol in contrast to the reaction with 5% Pd/C under the same conditions, which produced a mixture of 1,2-diphenylethanol and bibenzyl in an 85:15 ratio (entry 1). The stereochemistry of the other C−O bond was retained in the ring opening of (*R*,*R*)-2-methyl-3-phenyloxirane to give (*R*)-1-phenyl-2-propanol in 99% ee (entry 2). Esters and extra hydroxyl groups are compatible and do not disturb the regioselectivity (entries 3 and 4). As shown in the reaction of epichlorohydrin, **1** was also effective for the highly selective hydrogenolysis of aliphatic epoxides (entries 6 − 12). Generally, the reactions of aliphatic epoxide were slower than those of benzylic ones. For example, the hydrogenolysis of 2-hexyloxirane took 8 h in spite of increasing the amount of **1** 2-fold (2.0 mol % of Pd) (entry 6). However, exceptionally, the reaction of 1,2-epoxy-3-phenoxypropane was completed in 30 min by using 2.0 mol % of Pd (entry 7). The regioselectivity appeared to be governed by steric hindrance; the less hindered C−O bonds were cleaved in the reactions of terminal oxiranes. The selectivity was not affected by phenyloxy or hydroxyl group (entries 6 and 7). However, the reactions of 1,4-di(oxiran-2-yl)butane and 2-benzyloxirane were less selective to produce 1,8-octanediol and 3-phenyl-1-propanol as the minor products in 8% and 15% yield, respectively. The hydrogelnolysis of internal oxirane such as cyclohexene oxide was also successful to give cyclohexanol in 93% yield.

In summary, we have developed a simple process for preparing a magnetically separable and recyclable palladium catalyst by incorporating palladium nanoparticles and iron oxide nanoparticles in aluminum oxyhydroxide matrix and demonstrated its high activity in the selective hydrogenolysis of various epoxides at room temperature with a hydrogen balloon. Moreover, we have shown that the catalyst can be reused at least 25 times without loss of activity.

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Supporting Information Available: Experimental procedures, the magnetization curve for **1**, the photographs of reaction mixture, the NMR data for the products of epoxide hydrogenolysis, and the GC data for epoxides and the products of epoxide hydrogenolysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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[12] Palladium was not detected in the product by the inductively coupled plasma (ICP) analysis.