Palladium Nanoparticles Entrapped in Aluminum Hydroxide: Dual Catalyst for Alkene Hydrogenation and Aerobic Alcohol Oxidation
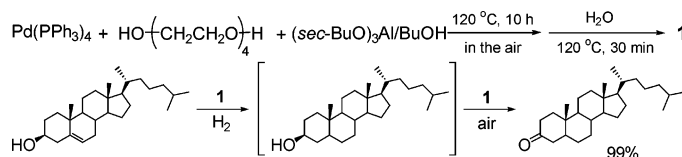
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ABSTRACT

A new aluminum hydroxide-supported palladium catalyst (1) made by a one-pot synthesis through nanoparticle generation and gelation shows a dual catalytic activity for olefinic hydrogenation and aerobic alcohol oxidation.

We report a new palladium catalyst that is highly active in both alkene hydrogenation and aerobic alcohol oxidation. To the best of our knowledge, this is the first report of such a catalyst that consecutively performs the two reactions in one pot. Furthermore, the catalyst is recyclable and amphiphilic, active in both water and common organic solvents.

Palladium nanoparticles have proved to be attractive catalysts in many useful transformations,[1] including the hydrogenation of alkenes and alkynes,[2] the oxidation of alcohols,[3] and carbon−carbon coupling reactions.[4]

Nanoparticles have been immobilized on inorganic solid supports[5] or embedded in organic polymers,[6] dendrimers,[7] multilayer polyelectrolyte films,[8] and ionic liquids for separation and reuse.[9] However, the immobilization often suffers from problems such as low reactivity, degradation, palladium leaching, and difficult synthetic procedures.

Very recently, we reported a simple one-pot method of making recyclable palladium catalysts through generation of palladium nanoparticles from $Pd(PPh_3)_4$ and tetra(ethylene glycol) dissolved in $(MeO)_4Si$ or $(i-PrO)_4Ti$ and subsequent gelation by treatment with water.[10] The resulting gels showed

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(1) (a) Negishi, E.-I. In *Handbook of Organopalladium Chemistry for Organic Synthesis*; Negishi, E., Ed.; John Wiley & Sons: New York, 2002. (b) Stahl, S. S. *Angew. Chem., Int. Ed.* **2004**, *43*, 3400.

(2) (a) Schlögl, R.; Hamid, S. B. A. *Angew. Chem., Int. Ed.* **2004**, *43*, 1628. (b) Roucoux, A.; Schulz, J.; Patin, H. *Chem. Rev.* **2002**, *102*, 3757. (c) Son, S. U.; Jang, Y.; Park, J.; Na, H. B.; Park, H. M.; Yun, H. J.; Lee, J.; Hyeon, T. *J. Am. Chem. Soc.* **2004**, *126*, 5026. (d) Thomas, J. M.; Johnson, B. F. G.; Raja, R.; Sankar, G.; Midgley, P. A. *Acc. Chem. Res.* **2003**, *36*, 20.

(3) Mallat, T.; Baiker, A. *Chem. Rev.* **2004**, *104*, 3037.

(4) (a) Jansat, S.; Gómez, M.; Philippot, K.; Muller, G.; Guiu, E.; Claver, C.; Castillón, S.; Chaudret, B. *J. Am. Chem. Soc.* **2004**, *126*, 1592. (b) Moreno-Mañas, M.; Pleixats, R. *Acc. Chem. Res.* **2003**, *36*, 638.

(5) (a) Choudary, B. M.; Madhi, S.; Chowdari, N. S.; Kantam, M. L.; Sreedhar, B. *J. Am. Chem. Soc.* **2002**, *124*, 14127. (b) Djakovitch, L.; Koehler, K. *J. Am. Chem. Soc.* **2001**, *123*, 5990.

(6) (a) Chauhan, B. P.; Rathore, J. S.; Chauhan, M.; Krawicz, A. *J. Am. Chem. Soc.* **2003**, *125*, 2876. (b) Biffis, A.; Zecca, M.; Basato, M. *J. Mol. Catal. A: Chem.* **2001**, *173*, 249.

(7) Ooe, M.; Murata, M.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *J. Am. Chem. Soc.* **2004**, *126*, 1604.

(8) Kidambi, S.; Dai, J.; Li, J.; Bruening, M. L. *J. Am. Chem. Soc.* **2004**, *126*, 2658.

(9) (a) Huang, J.; Jiang, T.; Gao, H.; Han, B.; Liu, Z.; Wu, W.; Chang, Y.; Zhao, G. *Angew. Chem., Int. Ed.* **2004**, *43*, 1397. (b) Dupont, J.; Fonseca, G. S.; Umpierre, A. P.; Fichtner, P. F. P.; Teixeira, S. R. *J. Am. Chem. Soc.* **2002**, *124*, 4228.

high catalytic activities in hydrogenation of alkenes and alkynes and in carbon−carbon cross-coupling reactions.

In this work, we used aluminum tri-*sec*-butoxide in place of $(MeO)_4Si$ or $(i\text{-}PrO)_4Ti$ and added 1-butanol to reduce the viscosity of the reaction mixture. A mixture of $Pd(PPh_3)_4$, tetra(ethylene glycol), 1-butanol, and aluminum tri-*sec*-butoxide was heated to generate palladium nanoparticles, and water was added to form a black gel (Scheme 1). Filtering,

Scheme 1. Preparation of the Palladium Catalyst
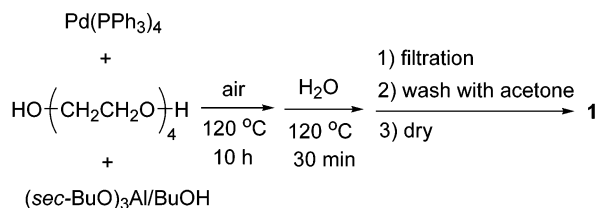
washing with acetone, and drying the gel gave **1** as dark olive-green powder.[11,12] Despite the seemingly minor change, the resulting catalyst showed quite remarkable catalytic activities, suggesting a crucial role of the aluminum hydroxide matrix.

The catalytic activity of **1** in hydrogenation was tested with cholesterol (Table 1). Although a smaller amount was used,

Table 1. Catalytic Hydrogenations of Cholesterol to Cholestanol[a]

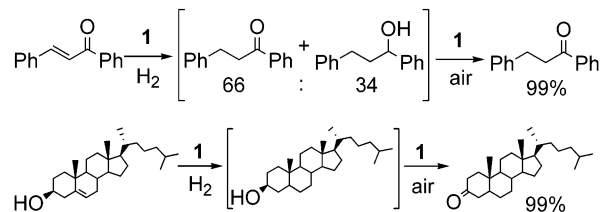| entry	catalyst (mol % Pd)	T (°C)	time (h)	yield (%)
1	**1** (2.0)	25	6	>99[b]
2[c]	$TiO_2/TEG/Pd$ (2.0)	25	24	16
3[d]	PI Pd (5)	25	24	63−85
4[e]	8% Pd/C (7.4)	50	50	100
5	**1**[f] (2.0)	25	6	>99[b]

[a] Hydrogenations were performed under atmospheric pressure. [b] Isolation yield. [c] Ref 10. [d] Ref 13. [e] Ref 14. [f] Recovered from the ninth use.

1 was more active than the titania-supported palladium catalyst,[10] the polymer incarcerated palladium,[13] and 8% Pd/C.[14] The activity of recycled **1** was also excellent: it could be recovered by simple filtration in the air and was reused 10 times without activity loss.[15]

Meanwhile, the hydrogenation of *trans*-chalcone with **1** at room temperature gave a 2:1 mixture of 1,4-diphenyl-2-

butanone and 1,4-diphenyl-2-butanol. Subsequently, we could convert the mixture to pure 1,4-diphenyl-2-butanone in 99% yield by exposing the mixture to the air while heating at 80 °C for 2 h. The dual activity of **1** was also effective in transforming cholesterol to cholestan-3-one (Scheme 2).

Scheme 2. Hydrogenation Followed by Aerobic Oxidation

The catalytic activity of **1** in aerobic oxidation was tested with 1-phenylethanol (Table 2). The oxidation of **1** was

Table 2. Catalytic Oxidation of 1-Phenylethanol[a]

entry	catalyst	mol % Pd	solvent	oxidant	T (°C)	time (h)	yield[b] (%)
1	1	0.2	toluene	air	80	6	>99
2	1	0.2	EtOAc	air	80	12	>99
3	1	0.2	TFT[c]	O_2	80	2	>99
4	1	1.0	H_2O	air	100	6	90
5[d]	1	0.005	none	air	150	35	98
6	Pd/C	2	toluene	air	80	6	9
7	Pd/Al_2O_3	0.5	toluene	air	80	6	31
8[e]	Ru/Al_2O_3	2.5	TFT[c]	O_2	83	1	99
9[f]	ARP−Pd	2	H_2O	O_2	100	20	99
10[g]	Pd/MgO	1.0	TFT[c]	O_2	70	8	45
11[h]	PdHAP-0	0.2	TFT[c]	O_2	90	1	98

[a] Oxidation was performed on 1.00 mmol of a substrate dissolved in 2 mL of solvent under atmospheric air or 1 atm O_2. [b] Determinied by GC. [c] TFT = trifluorotoluene. [d] Performed with 124 mg of **1** for 24 mL of 1-phenylethanol. [e] Ref 17. [f] Ref 16c. [g] Ref 18. [h] Ref 19.

performed under various conditions for comparison with the commercially available catalysts (Pd/C and Pd/Al_2O_3) and the recently reported heterogeneous catalysts. The aerobic oxidation of 1-phenylethanol proceeded smoothly with only 0.20 mol % Pd in conventional organic solvents. It also worked in water: **1** showed better activity than the recently reported resin-dispersed palladium nanoparticles in water.[16c] The amount of **1** could be reduced to 0.005 mol % Pd in solvent-free conditions, showing a high turnover frequency (TOF). **1** was more active than the commercially available Pd/C and Pd/Al_2O_3, the alumina-supported ruthenium catalyst,[17] and the magnesium oxide-supported palladium catalyst.[18] A hydroxyapatite-supported palladium catalyst (PdHAP-

(10) Kim, N.; Kwon, M. S.; Park, C. M.; Park, J. *Tetrahedron Lett.* **2004**, *45*, 7057.

(11) During the preparation of **1**, triphenylphosphine was oxidized into triphenylphosphine oxide, which was recovered from the filtrate in 97%. In addition, almost all of tetra(ethylene glycol) was found to be present in the filtrate in contrast to the cases with $(MeO)_4Si$ and $(i\text{-}PrO)_4Ti$.

(12) See Supporting Information for its characterization, including TEM images.

(13) Okamoto, K.; Akiyama, R.; Kobayashi, S. *J. Org. Chem.* **2004**, *69*, 2871.

(14) Kollár, L.; Tõrös, S.; Heil, B.; Tuba, Z. *J. Mol. Catal.* **1988**, *47*, 33.
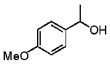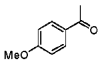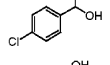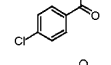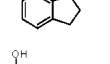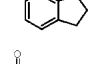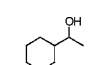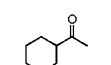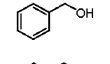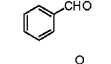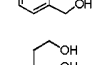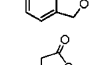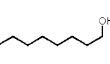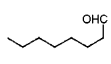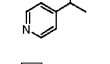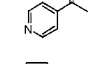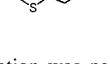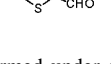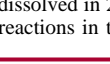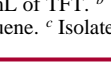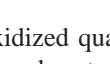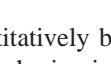
(15) Palladium was not detected in the product by the inductively coupled plasma (ICP) analysis.

(16) For the palladium-catalyzed aerobic oxidation of alcohols in water, see: (a) ten Brink, G.-J.; Arends, I. W. C. E.; Hoogenraad, M.; Verspui, G.; Sheldon, R. A. *Adv. Synth. Catal.* **2003**, *345*, 1341. (b) ten Brink, G.-J.; Arends, I. W. C. E.; Hoogenraad, M.; Verspui, G.; Sheldon, R. A. *Adv. Synth. Catal.* **2003**, *345*, 497. (c) Uozumi, Y.; Nakao, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 194.

0)[19] showed a greater TOF than **1**. However, PdHAP-0 required centrifugation for recovery and KCl or NaCl treatment for reuse, whereas **1** could be recovered readily by filtration and reused at least 10 times without activity loss.

The scope of aerobic alcohol oxidation by **1** was studied further with various alcohols (Table 3). Aromatic alcohols

Table 3. Catalytic Oxidation of Various Alcohols with **1**[a,b]

entry	substrate	product	mol % Pd	T (°C)	time (h)	yield[c] (%)
1			0.20 (0.50)	80 (80)	1 (6)	>99 (>99)
2			2.0 (2.0)	100 (110)	24 (45)	88 (87)
3			0.20 (0.50)	80 (80)	3 (6)	>99 (>99)
4			1.0 (2.0)	100 (110)	4 (20)	>99 (81)
5			1.0 (2.0)	100 (110)	10 (18)	94 (86)
6			(0.50)	(70)	(2)	(>99)
7			(0.50)	(80)	(12)	(99[d])
8			(2.0)	(110)	(16)	(99[d])
9			2.0 (2.0)	100 (110)	12 (12)	19 (<5)
10			5.0 (1.0)	100 (110)	14 (12)	92 (62)
11			5.0 (1.0)	100 (110)	18 (24)	90 (64)

[a] Oxidation was performed under atmospheric air on 1.00 mmol of a substrate dissolved in 2 mL of TFT. [b] Values in the parentheses are results from the reactions in toluene. [c] Isolated yield. [d] Determined by ¹H NMR.

were oxidized quantitatively by 0.5 mol % Pd at 80 °C in toluene under atmospheric air. The use of trifluorotoluene (TFT) significantly increased the oxidation rate. For instance,

the oxidation of 1-(4-methoxyphenyl)ethanol was completed within 1 h by 0.2 mol % Pd. A notable exception was 1-(4-chlorophenyl)-ethanol; 4-chloroacetophenone was obtained in only 88% yield even after 24 h at 100 °C by 2 mol % Pd in TFT. Aromatic alcohols were oxidized faster than aliphatic ones, and the secondary alcohols were oxidized faster than the primary ones. Aromatic and aliphatic primary 1,4-diols transformed to β-lactones quantitatively. However, **1** was not effective for the oxidation of primary aliphatic alcohols;[20] 1-octanol was oxidized in less than 5% under the conditions for the oxidation of 1,4-butanediol. Notably, **1** was effective for the oxidation of heteroaromatic alcohols such as 1-(3-pyridyl)ethanol and 2-(hydroxymethyl)thiophene. Satisfactory results were obtained by using 5 mol % Pd and TFT.

In summary, we have developed a simple synthetic method for an easily recyclable palladium catalyst from readily available reagents and demonstrated its high and dual activity in both hydrogenation of alkenes and aerobic oxidation of alcohols. We are investigating the basis of the distinctive catalytic activity of palladium nanoparticles supported by aluminum hydroxide.

Supporting Information Available: TEM images of **1** and experimental procedures for the synthesis of **1**, the hydrogenation of cholesterol, the aerobic oxidation of 1-phenylethanol, and the transformation of cholesterol to cholestan-3-one. This material is available free of charge via the Internet at http://pubs.acs.org.

OL047381W

(17) (a) Yamaguchi, K.; Mizuno, N. *Angew. Chem., Int. Ed.* **2002**, *41*, 4538. (b) Yamaguchi, K.; Mizuno, N. *Chem. Eur. J.* **2003**, *9*, 4353.

(18) Pillai, U. R.; Sahle-Demessie, E. *Green Chem.* **2004**, *6*, 161.

(19) Mori, K.; Yamaguchi, K.; Hara, T.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *J. Am. Chem. Soc.* **2002**, *124*, 11572.

(20) For recent reports for aerobic oxidation of primary alcohols, see: (a) Velusamy, S.; Ahamed, M.; Punnyamurthy, T. *Org. Lett.* **2004**, *6*, 4821. (b) Markó, I. E.; Gautier, A.; Dumeunier, R.; Doda, K.; Philippart, F.; Brown, S. M.; Urch, C. J. *Angew. Chem., Int. Ed.* **2004**, *43*, 1588. (c) Velusamy, S.; Punnyamurthy, T. *Org. Lett.* **2004**, *6*, 217.