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Acceptor-Free Alcohol Dehydrogenation by Recyclable Ruthenium Catalyst

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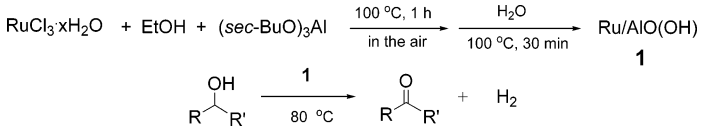
ABSTRACT



An efficient oxidant-free oxidation for a wide range of alcohols was achieved by a recyclable ruthenium catalyst. The catalyst was prepared from readily available reagents by a one-pot synthesis through nanoparticle generation and gelation.

Oxidation of alcohols to carbonyl compounds is a fundamental organic transformation.[1] To meet environmental and economical acceptability, much effort has been devoted to develop catalysts systems using molecular oxygen and hydrogen peroxide as the hydrogen acceptors.[2] However, their application to a large-scale production may be hindered by safety problems.[3] Although transfer dehydrogenation of alcohols using ketones and alkenes in anaerobic conditions can be an alternative method, acceptor-free alcohol dehydrogenation is ideal. Several homogeneous catalyst systems have been reported for the dehydrogenation, but they suffer from air sensitivity, low catalytic activity, harsh conditions, requirement of additives, and/or difficult catalyst synthesis and manipulation.[4−8]

Heterogeneous catalysts for the dehydrogenation, in general, have been developed mainly for the interest of hydrogen production from renewable biomass or its fermentation products.[4a] Our group has developed several catalyst systems for alcohol oxidation under aerobic and anaerobic conditions.[5,9b] Palladium nanoparticles in aluminum oxyhydroxide is a recent example for the aerobic alcohol oxidation, and an immobilized form of Shvo's diruthenium complex is for the anaerobic alcohol dehydrogenation without any additives.

Here, we describe a recyclable and easily makeable heterogeneous catalyst (**1**) for acceptor-free alcohol dehydrogenation (Scheme 1). It is active under mild conditions without additives for a wide range of alcohols including those having heteroatoms such as nitrogen and sulfur.

Recently, we have reported a simple synthetic method for recyclable metal nanoparticle catalysts through a sol−gel process,[9] which involves readily available reagents and does not require calcination nor sintering. The ruthenium catalyst

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(1) (a) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1984. (b) Hudlicky, M. *Oxidation in Organic Chemistry*; American Chemical Society: Washington, DC, 1990.

(2) (a) Sheldon, R. A.; Arends, I. W. C. E.; Dijksman, A. *Catal. Today* **2000**, *57*, 157. (b) Muzart, J. *Tetrahedron* **2003**, *59*, 5789. (c) Zhan, B.-Z.; Thompson, A. *Tetrahedron* **2004**, *60*, 2917. (d) Sheldon, R. A.; van Santen, R. A. *Catalytic Oxidations: Principles and Applications*; World Scientific: Singapore, 1995; p 239.

(3) (a) Keresszegi, C.; Mallat, T.; Baiker, A. *New J. Chem.* **2001**, *25*, 1163. (b) Zaccheria, F.; Ravasio, N.; Psaro, R.; Fusi, A. *Chem. Commun.* **2005**, 253.

(4) (a) Junge, H.; Beller, M. *Tetrahedron Lett.* **2005**, *46*, 1031. (b) Meijer, R. H.; Ligthart, G. B. W. L.; Meuldijk, J.; Vekemans, J. A. J. M.; Hulshof, L. A. *J. Mol. Catal. A* **2004**, *218*, 29.

(5) Choi, J. H.; Kim, N.; Shin Y. J.; Park, J. H.; Park, J. *Tetrahedron Lett.* **2004**, *45*, 4607.

(6) van Buijtenen, J.; Meuldijk, J.; Vekemans, J. A. J. M.; Hulshof, L. A.; Kooijman, H.; Spek, A. L. *Organometallics* **2006**, *25*, 873.

(7) Zhang, J.; Gandelman, M.; Shimon, L. J. W.; Rozenberg, H.; Milstein, D. *Organometallics* **2004**, *23*, 4026.

(8) Adair, G. R. A.; Williams, J. M. J. *Tetrahedron Lett.* **2005**, *46*, 8233.

(9) (a) Kwon, M. S.; Kim, N.; Seo, S. H.; Park, I. S.; Cheedrala, R. K.; Park, J. *Angew. Chem., Int. Ed.* **2005**, *44*, 6913. (b) Kwon, M. S.; Kim, N.; Park, C. M.; Lee, J. S.; Kang, K. Y.; Park, J. *Org. Lett.* **2005**, *7*, 1077. (c) Park, I. S.; Kwon, M. S.; Kim, N.; Lee, J. S.; Kang, K. Y.; Park, J. *Chem. Commun.* **2005**, 5667. (d) Kim, N.; Kwon, M. S.; Park, C. M.; Park, J. *Tetrahedron Lett.* **2004**, *45*, 7057.

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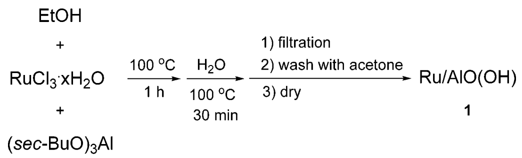
Scheme 1. Preparation of the Ruthenium Catalyst



1 was prepared from ruthenium(III) chloride hydrate, ethanol, and (*s*-BuO)$_3$Al through a procedure similar to those reported previously.[10] The TEM images for **1** showed a fibrous matrix typical for aluminum oxyhydroxide (Figure 1). Although ruthenium nanoparticles were not identified clearly in the TEM images, energy-dispersive X-ray analysis (EDX) and X-ray photoelectron spectroscopy (XPS) showed that ruthenium exists mainly as Ru(0) species in the matrix.[10]

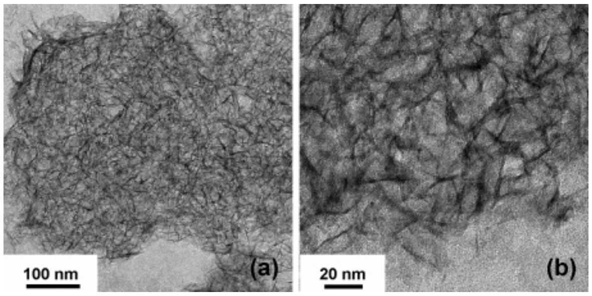


Figure 1. TEM image of **1**: (a) low resolution, (b) high resolution.

To find optimum conditions for alcohol dehydrogenation, 1-phenylethanol was dehydrogenated under various conditions. And the results were compared with that from the reaction with commercially available Ru/Al$_2$O$_3$ and with those reported previously for acceptor-free alcohol dehydrogenation (Table 1).

The reaction rate depended on catalyst amount and temperature; complete conversion to acetophenone was achieved in 24 h at 80 °C with 1.5 mol % of Ru, while it took 10 h with 3.0 mol % of Ru and 7 h at 110 °C with 3.0 mol % of Ru.[11] The dehydrogenation was possible without solvent and completed in 36 h with only 0.3 mol % of Ru at 150 °C (entry 4). Notably, **1** can be recovered by simple filtration and it remained active, even in the tenth use.[12] The effect of air was not significant for the dehydrogenation with **1** (entry 6).

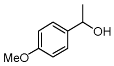
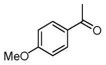
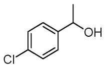
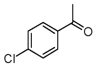
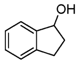
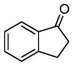
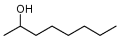
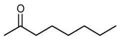
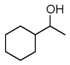
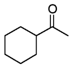
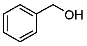
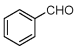
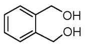
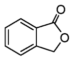
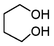
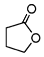
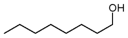
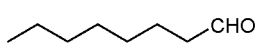
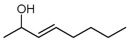
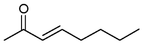
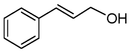
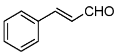
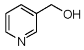
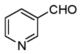
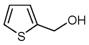
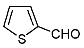
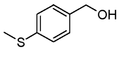
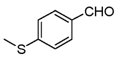
In comparison to a commercial ruthenium catalyst (Ru/Al$_2$O$_3$), **1** showed at least five times higher activity. Compound **1** was also much more active than the homoge-

Table 1. Catalytic Dehydrogenation of 1-Phenylethanol[a]

entry	catalyst (mol % of Ru)	T (°C)	time (h)	yield[b] (%)
1	**1** (1.5)	80	10	69
2			24	>99
3	**1** (3.0)	80	5	71
4			10	>99
5	**1** (3.0)	110	5	90
6			7	>99
7	**1** (0.3)[c]	150	36	>99
8	**1** (3.0)[d]	80	10	96
9	**1** (3.0)[e]	80	8	>99
10	5% Ru/Al$_2$O$_3$ (3.0)[f]	80	10	21
11	[(η^5-Ph$_4$C$_4$CO)$_2$H]Ru$_2$-((CO)$_4$)(μ-H)(4.0)[g]	110	9	81
12	[Ru(μ-OCOC$_2$F$_4$OCO)(CO)-(H$_2$O)(BINAP)]$_2$ (0.5)[h]	100	92	93
13	(PNP)Ru(H)Cl(N$_2$) (0.4)[i]	100	100	64
14	PhCH=Ru(PCy$_3$)$_2$Cl$_2$ (5.0)[j]	110	24	6

[a] The dehydrogenations were performed under argon on 0.20 mmol of 1-phenylethanol dissolved in 1.0 mL of dry toluene. [b] Determined by GC. [c] Without solvent, 1 mL of 1-phenylethanol was emloyed. [d] Recovered from the ninth use. [e] In the air. [f] Purchased from Acros. [g] Reference 5. [h] Reference 6. [i] Reference 7. [j] Reference 8.

Table 2. Catalytic Dehydrogenation of Various Alcohols with **1**[a]

entry	substrate	product	mol % Ru	T (°C)	time (h)	yield (%)[b]
1			3.0	80	8	>99
2			4.5	110	36	>99
3			3.0	80	20	>99
4			4.5	110	15	>99
5			4.5	110	12	99
6			3.0	80	5	>99
7			3.0	80	12	98
8			6.0	110	32	94
9			6.0	110	24	23[c]
10			6.0	110	10	97
11			6.0	110	12	93
12			6.0	110	36	80
13			3.0	80	5	97
14			3.0	110	20	95

[a] The dehydrogenation was performed under argon on 1.0 mmol of a substrate dissolved in 5.0 mL of dry toluene. [b] Isolated yield. [c] Determined by GC using dodecane as the internal standard.

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

(11) 1-Phenylethanol was not detected in the hydrogenation of acetophenone with hydrogen (1 atm) and **1** (4.0 mol % of Ru) at 80 °C in 10 h.

(12) Ruthenium was not detected in the product obtained from the tenth use by the inductively coupled plasma (ICP) analysis. The yields in the reuse are following: (1) >99%; (2) >99%; (3) 98%; (4) 99%; (5) >99%; (6) 97%; (7) 96%; (8) 97%; (9) 97%.

neous catalysts reported recently, which include the Shvo catalyst,[5] a diruthenium complex containing dicarboxylate and phosphine ligands,[6] a ruthenium PNP-type complex,[7] and the Grubbs catalyst.[8]

The scope of alcohol dehydrogenation by **1** was studied with benzylic alcohols, aliphatic ones, and those containing heteroatoms such as nitrogen and sulfur (Table 2).

High-yield dehydrogenation was achieved for aliphatic alcohols as well as for benzylic ones. Generally, benzylic alcohols were dehydrogenated faster than aliphatic ones. For example, the dehydrogenation of 1-(4-methoxyphenyl)-ethanol was completed in 8 h at 80 °C with 3.0 mol % of Ru, while that of 2-octanol required 15 h at 110 °C with 4.5 mol % of Ru. Exceptions were 1-(4-chlorophenyl)ethanol and 3-pyridylcarbinol; it took 36 h at 110 °C with 4.5 mol % of Ru for the complete conversion to 4-chloroacetophenone, and nicotinaldehyde was obtained only in 80% yield after 36 h at 110 °C with 6.0 mol % of Ru. 1,4-Butanediol as well as 1,2-beneznedimethanol transformed to the corresponding γ-lactones in high yields. However, the reaction of 1-octanol produced a complex mixture containing 1-octanal only in 23% after 24 h at 110 °C with 6.0 mol % of Ru.[13] Allylic alcohols transformed to the corresponding $\alpha,\beta-$unsaturated carbonyl compounds selectively. Compound **1** was also effective for the dehydrogenation of alcohols containing heteroatoms such as 3-pyridylcarbinol, 2-(hydroxymethyl)thiophene, and 4-(methylthio)benzyl alcohol.

In conclusion, we have demonstrated a highly efficient catalytic alcohol dehydrogenation, not requiring acceptors and additives. The dehydrogenation is effective for benzylic alcohols, aliphatic ones, and heteroatom-containing ones. The catalyst is readily makeable, easily recoverable, and reusable at least 10 times without activity loss.

Acknowledgment. This work was supported by a Korea Research Foundation Grant (KRF-2005-005-C00007).

Supporting Information Available: Experimental procedures for the synthesis of **1**, the dehydrogenation of 1-phenylethanol, and the characterization data for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[13] More than four peaks were observed, but the production of octyl octanoate was negligible.