Copper nanoparticles on hydrotalcite as a heterogeneous catalyst for oxidant-free dehydrogenation of alcohols†

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We have developed a highly efficient heterogeneous catalytic system using hydrotalcite-supported Cu nanoparticles (Cu/HT) that can successfully promote the oxidant-free dehydrogenation of various alcohols under liquid-phase conditions.

Alcohol oxidation is a key reaction in both academic and industrial synthetic chemistry. Recently, oxidant-free alcohol dehydrogenation[1] has received considerable attention because it has the advantages of being able to prevent overoxidation of aldehyde functionalities and also of eliminating the formation of water as a by-product, which could lead to catalyst deactivation and the hydrolysis of ester and ether moieties in the substrate. We recently developed Ag nanoparticles on hydrotalcite (Ag/HT)[2,3] as a heterogeneous and reusable catalyst for the efficient oxidant-free dehydrogenation of various alcohols. The activity of Ag/HT is comparable to those of previously reported catalysts such as Pd,[4] Pt,[5] Ru[6] and Au,[7] which have achieved high performance for various alcohols using molecular oxygen as the oxidant. From ecological and practical points of view, the development of a reusable and less expensive base-metal catalyst is highly desirable.

Herein, we reveal that Cu nanoparticles grafted on hydrotalcite (Cu/HT) exhibit high catalytic activity for the dehydrogenation of various alcohols, including less reactive cyclohexanols, without using any oxidant additives under liquid phase conditions. This Cu/HT catalyst has the advantages of eliminating the need to use high temperatures,[8] additives,[9] and high catalyst loading[10] that have plagued previously reported Cu catalysts. Moreover, Cu/HT is reusable while maintaining both high activity and selectivity.

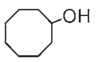
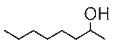
The HT (1.0 g) was synthesized by the co-precipitation method according to literature procedures.[11] The HT (1.0 g) was added to a solution of 0.8 mmol of copper(II) trifluoromethanesulfonate in 50 mL of deionized water, then the pH was adjusted to 8.0 with a solution of ammonia (25 wt%). After stirring the mixture for 1 h at 25 °C, the obtained solid was filtered, washed with deionized water, and dried *in vacuo* overnight at 25 °C, yielding the HT-supported copper(II) compound (Cu^{II}/HT) as a blue powder. This Cu^{II}/HT was dried *in vacuo* at 180 °C for 0.5 h and then reduced with 1 atm of molecular hydrogen (H_2) at 180 °C for 0.5 h, which afforded HT-supported Cu catalyst (Cu/HT) as a black powder. The formation of a Cu(0) species was confirmed (Fig. 1S, ESI†) from the Cu K-edge X-ray absorption fine-structure spectrum (XAFS). Cu/MgO, Cu/Al_2O_3, Cu/SiO_2, Cu/TiO_2 and Cu/Hydroxyapatite (HAP) were also prepared by similar procedures.

The Cu loading of Cu/HT is 4.6 wt% from elemental analysis. The mean diameter and standard variation of the Cu particles were, respectively estimated to be 7.5 and 4.3 nm from transmission electron microscopy (Fig. 2S, ESI†).

Initially, the oxidation of cyclooctanol to cyclooctanone using Cu/HT was examined as a model reaction. The dehydrogenation occurred under Ar atmosphere at 130 °C for 3 h, giving cyclooctanone in 99% yield together with the generation of H_2 (Table 1, entry 1). An almost equimolar amount of H_2 to cyclooctanone was confirmed during the course of the dehydrogenation. The use of other inorganic materials supporting Cu such as Cu/MgO, Cu/Al_2O_3, Cu/HAP, Cu/TiO_2, and Cu/SiO_2 also gave high yields of cyclooctanone (entries 2–6). Further screening of the above Cu catalysts using 2-octanol revealed that HT is the best support (entries 7–12).

We next investigated the catalytic activity of Cu/HT in the dehydrogenation of various alcohols as summarized in Table 2. Aliphatic and benzylic secondary alcohols were smoothly oxi-

Table 1 Dehydrogenation of alcohols using various Cu catalysts[a]

Entry	Substrate	Catalyst[b]	*t*/h	Conv.[c] (%)	Sel.[c] (%)
1		Cu/HT	3	>99	>99
2		Cu/MgO		83	>99
3		Cu/Al_2O_3		89	93
4		Cu/HAP		82	99
5		Cu/SiO_2		86	99
6		Cu/TiO_2		82	>99
7		Cu/HT	6	97	99
8		Cu/MgO		59	93
9		Cu/Al_2O_3		96	93
10		Cu/HAP		43	93
11		Cu/SiO_2		56	98
12		Cu/TiO_2		42	88

[a] *Reaction conditions*: alcohol (1.0 mmol), Cu catalyst (Cu: 7.3 mol%), *p*-xylene (5 mL), Ar. [b] Cu/HT (4.6 wt%), Cu/MgO (5.0 wt%), Cu/Al_2O_3 (4.9 wt%), Cu/SiO_2 (4.7 wt%), Cu/TiO_2 (4.9 wt%), Cu/HAP (5.3 wt%). [c] Determined by GC using an internal standard technique.

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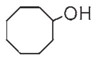
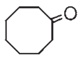
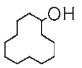
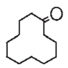
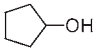
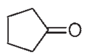
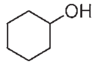
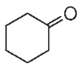
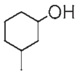
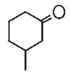
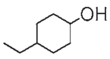
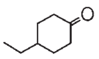
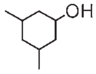
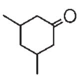
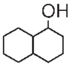
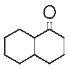
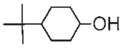
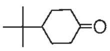
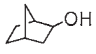
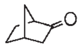
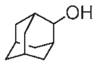
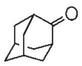
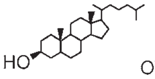
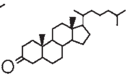
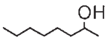
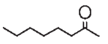
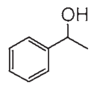
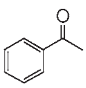
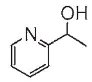
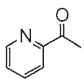
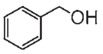
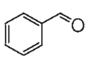
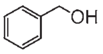
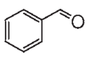
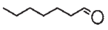
† Electronic supplementary information (ESI) available: XAFS and TEM analysis. See DOI: 10.1039/b809012b

Table 2 Alcohol dehydrogenation catalyzed by Cu/HT[a]

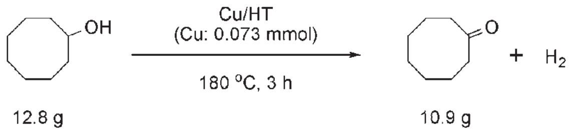
Entry	Substrate	Product	T/°C	t/h	Conv.[b] (%)	Sel.[b] (%)
1			130	3	>99	>99
2	1st reuse		130	3	99	94
3	2nd reuse		130	3	99	96
4			130	4	>99	93
5			130	3	99	33[c]
6			140	18	99	94
7[d]			140	8	86	80
8[e]			140	24	95	>99
9[d]			140	5	84	90
10[e]			150	24	82	95
11[d]			140	5	72	93
12[e]			150	12	83	>99
13[d]			140	8	94	88
14[e]			150	24	93	>99
15[d]			160	6	96	72
16[e]			150	24	98	85
17[d]			150	9	99	97
18[e]			150	9	95	98
19[f]			150	24	99	94
20[fg]			150	17	84	96
21			130	6	97	99
22			130	3	98	99
23			130	17	84	96
24			130	9	60	92
25[h]			130	13	85	69[i]
26			130	12	19	47

[a] *Reaction conditions*: alcohol (1.0 mmol), Cu/HT (7.3 mol%), *p*-xylene (5 mL), Ar. [b] Determined by GC using an internal standard technique. [c] Aldol product was formed as a by-product. [d] Alcohol (0.5 mmol), Cu/HT (14 mol%). [e] Cu/HAP (14 mol%). [f] Mesitylene (5 mL). [g] Alcohol (0.20 mmol). [h] Alcohol (0.3 mmol). [i] Benzyl benzoate was formed as a by-product.

dized to give the corresponding ketones in high yields, and the Cu/HT was also effective for a bulky alcohol and a heterocyclic alcohol including a nitrogen atom (entries 20 and 23). Unfortunately, the dehydrogenation of primary alcohols gave the corresponding aldehydes in moderate yields (entries 24 and 26). In the case of benzyl alcohol, the yields of benzaldehyde were not improved, despite prolonging the reaction time, due to the formation of an ester of benzyl benzoate (entry 25). It is notable that alicyclic alcohols showed high reactivity for the dehydrogenation (entries 1–20) except for cyclopentanol where an aldol adduct of 2-cyclopentylcyclopentanone was formed as a by-product caused by the basic sites of HT (entry 5). Further, cyclohexanol, which is known to be a less reactive substrate even for the oxidation by precious metals such as Pd and Ru under molecular oxygen, was smoothly converted to give cyclohexanone in high yield (entry 6). Moreover, Cu/HT was broadly applicable to reactions with a wide range of cyclohexanol derivatives and only small amounts of aldol condensation products were generated. The use of neutral HAP supporting Cu (Cu/HAP) instead of Cu/HT achieved high selectivity for ketones while suppressing the formation of the aldol products (entries 8, 10, 12, 14, 16, 18).

This Cu/HT catalyst could also function in alcohol dehydrogenations under neat conditions (Scheme 1). A 100 mmol-scale dehydrogenation of cyclooctanol without solvent gave an 85% yield of cyclooctanone. The turnover number (TON) reached 1164 after 3 h [turnover frequency (TOF): 388 h^{-1}]. These TON and TOF values are remarkably higher than those reported for other heterogeneous Cu catalyst systems with or without hydrogen acceptors.[12]

After about 50% conversion of cyclooctanol, Cu/HT was filtered off at the reaction temperature, and further stirring of the filtrate under similar reaction conditions did not afford any dehydrogenation products. No Cu ions in the filtrate were detected by inductively coupled plasma (ICP) analysis (detection limit: 0.054 ppm). These results reveal that the present



Scheme 1 A 100 mmol-scale dehydrogenation of cyclooctanol under neat conditions.

alcohol dehydrogenation clearly took place on the Cu nanoparticles located on the HT surface. Furthermore, Cu/HT could be recycled twice in the dehydrogenation of cyclooctanol with retention of its activity and selectivity, giving 93% yield of cyclooctanone on the 1st reuse, and 95% on the 2nd reuse.

In conclusion, we have shown that Cu nanoparticles grafted on HT are highly active heterogeneous catalysts for acceptor-free dehydrogenation of various alcohols including less reactive cyclohexanol derivatives. This inexpensive base-metal catalyst was easily reusable and effective under neat conditions.

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Notes and references

1 R. Karvembua and S. Priyaregab, *React. Kinet. Catal. Lett.*, 2006, **88**, 333; W.-H. Kim, I. S. Park and J. Park, *Org. Lett.*, 2006, **8**, 2543; K. Fujita, N. Tanino and R. Yamaguchi, *Org. Lett.*, 2007, **9**, 109; J. van Buijtenen, J. Meuldijk, J. A. J. M. Vekemans, L. A. Hulshof, H. Kooijman and A. L. Spek, *Organometallics*, 2006, **25**, 873; J. Zhang, M. Gandelman, L. J. W. Shimon, H. Rozenberg and D. Milstein, *Organometallics*, 2004, **23**, 4026; J. H. Choi, N. Kim, Y. J. Shin, J. H. Park and J. Park, *Tetrahedron Lett.*, 2004, **45**, 4607; G. R. A. Adair and J. M. J. Williams, *Tetrahedron Lett.*, 2005, **46**, 8233; J. Zhang, M. Gandelman, L. J. W. Shimon and D. Milstein, *Dalton Trans.*, 2007, 107; G. B. W. L. Ligthart, R. H. Meijer, M. P. J. Donners, J. Meuldijk, J. A. J. M. Vekemans and L. A. Hulshof, *Tetrahedron Lett.*, 2003, **44**, 1507.

2 T. Mitsudome, Y. Mikami, H. Funai, T. Mizugaki, K. Jitsukawa and K. Kaneda, *Angew. Chem., Int. Ed.*, 2008, **47**, 138.

3 HT is a multifunctional material which has a cation-exchange ability in the brucite layer, an anion-exchange ability in the interlayer, and a tunable basicity of the surface. See: K. Ebitani, K. Motokura, T. Mizugaki and K. Kaneda, *Angew. Chem., Int. Ed.*, 2005, **44**, 3423; M. J. Climent, A. Corma, S. Iborra and A. Velty, *J. Catal.*, 2004, **221**, 474; K. Motokura, D. Nishimura, K. Mori, T. Mizugaki, K. Ebitani and K. Kaneda, *J. Am. Chem. Soc.*, 2004, **126**, 5662; B. M. Choudary, M. L. Kantam, A. Rahman, C. V. Reddy and K. K. Rao, *Angew. Chem., Int. Ed.*, 2001, **40**, 763; K. Yamaguchi, K. Mori, T. Mizugaki, K. Ebitani and K. Kaneda, *J. Org. Chem.*, 2000, **65**, 6897; B. Sels, D. DeVos, M. Buntinx, F. Pierard, A. K.-D. Mesmaeker and P. A. Jacobs, *Nature*, 1999, **400**, 855.

4 K. Mori, T. Hara, T. Mizugaki, K. Ebitani and K. Kaneda, *J. Am. Chem. Soc.*, 2004, **126**, 10657.

5 Y. Yoichi, A. Yamada, T. Arakawa, H. Hocke and Y. Uozumi, *Angew. Chem., Int. Ed.*, 2007, **46**, 704.

6 K. Yamaguchi, K. Mori, T. Mizugaki, K. Ebitani and K. Kaneda, *J. Am. Chem. Soc.*, 2000, **122**, 7144.

7 A. Abad, P. Concepción, A. Corma and H. García, *Angew. Chem.*, 2005, **117**, 4134; D. I. Enache, J. K. Edwards, P. Landon, B. S. Espriu, A. F. Carley, A. A. Herzing, M. Watanabe, C. J. Kiely, D. W. Knight and G. J. Hutchings, *Science*, 2006, **311**, 362.

8 M. Isamu (Nippon Shokubai Kagaku Kogyo), *JP Pat.*, 11335315, 1999.

9 J. Thorsten, L. Oliver, B. E. Johannes, E. Klaus, H. Klaus and W. Christian (BASF), *US Pat.*, 0191644, 2007.

10 H. L. Slaugh (Shell), *US Pat.*, 4891446, 1990.

11 F. Cavani, A. Trifiró and A. Vaccari, *Catal. Today*, 1991, **11**, 173.

12 F. Zaccheria, N. Ravasio, R. Psaro and A. Fusi, *Chem.–Eur. J.*, 2006, **12**, 6426 (TON = 6, TOF = 12); G. Ragagnin, B. Betzemeier, S. Quici and P. Knochel, *Tetrahedron*, 2002, **58**, 3985 (TON = 43).