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Synthetic Scope of Alcohol Transfer Dehydrogenation Catalyzed by Cu/Al_2O_3: A New Metallic Catalyst with Unusual Selectivity

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Abstract: A method for the anaerobic oxidation of a wide series of alcohols including cyclohexanols and steroidal alcohols, has been set up. It relies on a transfer dehydrogenation reaction from the substrate alcohol to styrene catalyzed by a heterogeneous, reusable copper catalyst under very mild liquid-phase experimental conditions (90 °C, N_2) and shows unusual selectivity. Thus, the method is selective for the oxidation of secondary and allylic alcohols even in the presence of unprotected primary and benzylic alcohols. Electronic effects and the choice of the hydrogen acceptor account for the selectivity observed.

Keywords: alcohols • dehydrogenation • heterogeneous catalysis • hydrogen transfer • oxidation

Introduction

The oxidation of alcohols to carbonyl compounds is an essential functional-group transformation in organic synthesis. Countless methods have been developed to perform this reaction, the most popular represented by the Collins,[1] Jones,[2] pyridinium chlorochromate (PCC),[3] pyridinium dichromate,[4] and Swern[5] oxidations. Most of these methods suffer from the use of stoichiometric toxic reagents, cryogenic conditions, and/or the production of copious amounts of waste.

An alternative approach is the use of a catalyst in combination with a stoichiometric oxidant, for example, tetrapropylammonium perruthenate (TPAP) with stoichiometric *N*-methylmorpholine (NMO),[6] while the use of supported[7,8] or unsupported[9] stable nitroxyl free radical precursor TEMPO (TEMPO = tetramethylpiperdinyloxy free radical) and of hypervalent iodine reagents[10] are an alternative to metal based oxidants.

Much more attractive is the use of molecular oxygen or air as the terminal oxidant, therefore the development of catalysts for the aerobic oxidation of alcohols has been explored by using a wide variety of metals. Very active copper based homogeneous systems have been setup,[11] whereas the heterogeneous systems mainly rely on the use of noble metals.[12]

An interesting alternative to aerobic conditions is represented by the use of a readily available organic molecule instead of oxygen as the hydrogen acceptor, thus overcoming safety concerns linked with the use of flammable solvents. However, only few cases of alcohol transfer dehydrogenation promoted by heterogeneous catalysts are known. Recently three palladium-based systems have been reported by Hayashi[13,14] and Baiker,[15] both active only in the oxidation of aromatic or allylic alcohols and one based on Ru.[16]

We recently reported that a low loading supported copper catalyst, 8% Cu/Al_2O_3, is very effective in selective oxidation of nonactivated aliphatic secondary alcohols under hydrogen-transfer dehydrogenation conditions.[17] Here we wish to report some additional results together with a mechanistical investigation on this catalytic system.

Results and Discussion

Copper catalysts prepared through a nonconventional chemisorption-hydrolysis technique have been shown to be active and very selective in a wide range of reductions, not only under catalytic hydrogenation conditions but also in hydrogen transfer reactions from secondary alcohols. In particular, Cu/Al_2O_3 was shown to be the most active reagent in transferring hydrogen from 2-propanol to 4-*tert*-butylcyclohexanone (Scheme 1). A detailed study aimed to elucidate the

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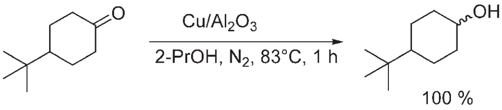


Scheme 1.

effect of the donor alcohol structure revealed the existence of a two-step mechanism based on the dehydrogenation of the donor followed by substrate reduction.[18]

In particular when (iPr)$_2$CHOH and 3-octanol were used as hydrogen donors, formation of the corresponding ketones was observed also after complete conversion of 4-*tert*-butylcyclohexanone. Moreover the stereochemistry observed in diisopropylcarbinol was coincident with that obtained under catalytic hydrogenation conditions, strongly suggesting that hydrogen availability on the catalyst surface is comparable both in the presence of molecular H$_2$ and when using this particular alcohol as a donor.

These results and the need for heterogeneous and simple systems for the oxidation of hydroxyl groups under liquid-phase conditions prompted us to investigate the activity of these copper catalysts in alcohol dehydrogenation reactions.

From the results catalysts Cu/SiO$_2$ and Cu/Al$_2$O$_3$ seemed promising, although in the absence of an acceptor an equilibrium situation between dehydrogenation and hydrogenation was reached. On the other hand if hydrogen is spilled off from the reactor (Table 1) it is apparent that the dehydrogenation reaction can go to completion. No reaction occurred in the presence of Al$_2$O$_3$ alone, although under these conditions the support showed some activity in hydrogen-transfer reactions from 2-propanol.[19]

Table 1. Oxidation of 3-octanol with different 8% Cu catalysts.[a]

Entry	Catalyst	t [h]	Conversion [%]	Selectivity [%]
1	Cu/SiO$_2$	20	100	100
2	Cu/Al$_2$O$_3$	12	84	100
3	Cu/MgO	20	40	100

[a] Reaction carried out by spilling-off H$_2$ from the reactor.

However, Cu/MgO, which showed activity comparable with that of Cu/SiO$_2$ in the transfer hydrogenation of 4-*tert*-butylcyclohexanone from 2-propanol, is scarcely active in 3-octanol dehydrogenation (entry 3), thus confirming once more that its activity in the former reaction is due mainly to a MPV-type mechanism (MPV = Meerwein–Ponndorf–Verley) and not to its dehydrogenation ability.[18]

To improve the synthetic potential of this reaction it seemed more effective to adopt transfer dehydrogenation conditions by exploiting a pivotal feature of these catalytic systems already expressed in other synthetic applications,[20,21] that is, their specificity towards hydrogenation of a conjugated system in the presence of an isolated one. Thus, by adding styrene in an equimolar ratio with respect to the substrate as a hydrogen acceptor, complete oxidation of the desired alcohol was obtained in very short reaction times, particularly over Cu/Al$_2$O$_3$. The byproduct, ethylbenzene, is easily removed from the reaction mixture together with the solvent. The catalyst was pretreated in H$_2$ at 543 K before use to reduce all the copper to the metallic phase; however, reduction at a much lower temperature (Table 2, entry 1b) still resulted in a very active material . On the contrary a lower copper loading on the catalyst results in much lower activity (entry 1a versus 1d and 21a versus 21b).

Three main features are apparent from the results reported in Table 2: the uncomplete conversion of benzylic alcohol (entry 5), the inactivity of primary alcohols (entries 3 and 7), and the high activity for secondary unactivated alcohols.

This trend is very different from that observed over almost all the oxidation catalytic systems reported so far, both based on a metal and on a radical precursor, which always convert benzylic alcohols faster than the other alcohols, thus suggesting that a different mechanism is operating in the present case.

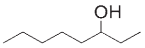
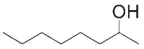
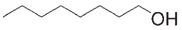
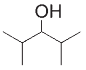
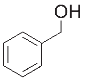
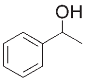
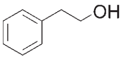
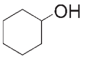
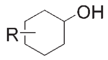
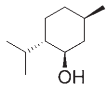
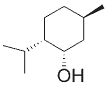
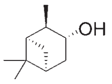
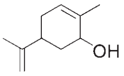
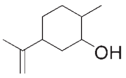
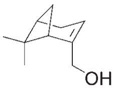
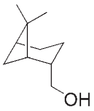
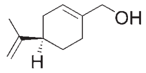
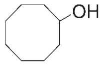
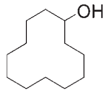
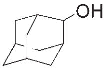
However, in total analogy with the Ru/Al$_2$O$_3$ systems,[22] the plot of $\log(k_X/k_H)$ versus the Brown–Okamoto σ^+ for a series of different benzylic alcohols was found to be linear with a slope corresponding to a Hammett $\rho+$ value of -0.75 ($r^2 = 0.97$), while the correlation with the σ^+ is better than that with σ constants, particularly for electron donating substituents (Figure 1, Table 3). This shows that the formation of a carbocation-type transition state is involved in the oxidation path. Therefore benzylic alcohols should exhibit the fastest reaction rates, owing to the higher stability of their corresponding carbocations. The uncomplete conversion observed under our experimental conditions can thus be ascribed to the inadequacy of the hydrogen acceptor used, which is unable to prevail over the aromatic aldehyde formed.

This apparent drawback, however, also has a plus side as it allows us to finely-tune the system selectivity. Thus, the competitive dehydrogenation of cyclooctanol and benzyl alcohol shows a marked selectivity towards the oxidation of the secondary alcohols (Figure 2), but in the absence of styrene, benzaldehyde acts as the acceptor and oxidation of cyclooctanol becomes specific (Figure 3).

The large decrease in the rate of cyclooctanol disappearance during competitive dehydrogenation and the small reduction in the rate of benzyl alcohol oxidation are strong evidence that the latter compound displaces cyclooctanol from the catalyst surface.[23] This is why benzaldehyde or substituted benzaldehydes may well be used as the acceptor, as shown by a test carried out on cyclooctanol (Table 2, entry 21c), but with a dramatic decrease in reaction rate.

It is worth underlining that this is the only case in which the product competes with the acceptor, as even secondary benzylic alcohols can be readily oxidized notwithstanding the high activity of Cu/Al$_2$O$_3$ in the hydrogenation of aromatic ketones[24] (entry 6). The effectiveness of styrene with respect to aromatic ketones in trapping the hydrogen formed is also shown by the dehydrogenation of optically pure (R)-1-phenyl-ethanol which proceeds without racemization with up to 80% conversion.

Table 2. Transfer dehydrogenation of different alcohols over Cu/Al_2O_3.

Entry		Substrate	t [h]	Conversion [%]	Selectivity [%]
1	a		1.5	100	100
	b		2.5[a]	98	100
	c		2.5[b]	97	100
	d		4[c]	96	100
2			4	100	100
3			24	4	100
4			6	100	100
5			20	51.5	100
6			0.75	100	100
7			24	1	100
8			3	99	98
9	R = 2-Me		3.5	99	100
10	R = 3-Me		3	100	100
11	R = 4-Me		1.5	100	100
12	R = 4-*t*Bu		1.5	97	100
13			48	50[d]	100
14			6	97[d]	100
15			48	40[d]	100
16	a		2.5	100	88
	b		1.5[e]	100	95
17			30	95	91
18			2	93	84
19			30	15	100
20			6	95	91
21	a		0.5	100	100
	b		1[c]	90	100
	c		9[f]	90	100
22			2	97	100
23			1.5	100	100

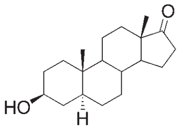
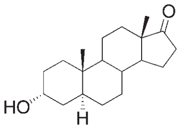
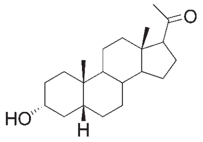
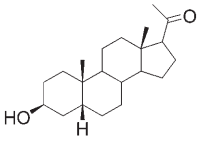
Steric effects also play a significant role. This is apparent in the monosubstituted cyclohexanols series (entries 9–12), in the very low activity of isopinocampheol (entry 15), and from the comparison between linear and branched substrates (entry 1 versus 4). This effect is so strong that in disubstituted cyclohexanols the reaction takes place at a reasonable rate only when the OH group is in axial conformation, as shown by the comparison of (−)-menthol with neomenthol (entry 13 versus 14).

For the same reason in 3-sterols the oxidation is faster when the OH group is in the 3β-position both in the 5α (entry 24 versus 25) and 5β series (entry 26 versus 27). This shows that the OH group has to be as unhindered as possible to effectively adsorb on the catalyst surface.

According to the relevant literature on the mechanism of secondary alcohols dehydrogenation over metallic copper catalysts, a proper orientation of the alcohol molecule on the surface is required.[25–27] In particular, Rioux and Vannice suggested that formation of a hydrogen molecule from isopropanol occurs in two sequential elementary steps and that the first hydrogen atom removed is the hydroxyl one. Even though the O−H bond is stronger than the C−H one, its cleavage prior to the α hydrogen is attributed to its orientation on the surface of copper on carbon catalysts.[25] We suggest that this also holds for the Cu/Al_2O_3-catalyzed reaction. After this step, the richer the incipient carbenium ion in the electrons the fastest will be the remotion of the second hydrogen atom from the α carbon.

The understanding of the strong electronic effects operating in this catalytic system and

Table 2. (Continued)

Entry	Substrate	t [h]	Conversion [%]	Selectivity [%]
24		2.5	100	96
25		4	86	100
26		24	41	75
27		5	89	80

[a] Catalyst activated at 453 K. [b] Ethylbenzene as solvent. [c] Catalyst with 5% Cu loading. [d] Mixture of ketone diastereoisomers. [e] Substrate/styrene = 1:2. [f] Benzaldehyde as hydrogen acceptor.

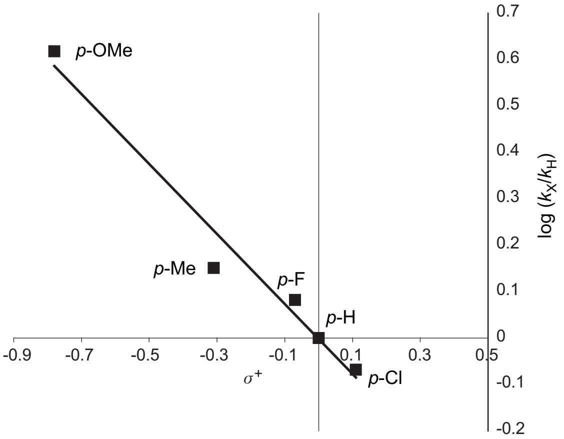
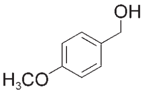
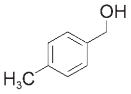
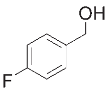
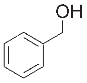
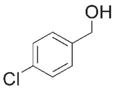


Figure 1. Hammett plot for competitive dehydrogenation of benzyl alcohol and p-substituted benzyl alcohols. Reaction conditions: benzyl alcohol (0.5 mmol), p-substituted benzyl alcohol (0.5 mmol), styrene (1 mmol), 8% Cu/Al_2O_3 (100 mg), toluene (8 mL), 363 K, N_2 atmosphere. No suitable data are available for the reaction of p-NO_2-benzyl alcohol due to poisoning of the catalyst in the presence of the nitro group.[24]

Table 3. Oxidation of substituted benzylic alcohols.

Entry	Substrate	t [h]	Conversion [%]
1		20	80
2		20	57
3		20	52
4		20	49
5		20	33

of the role played by the acceptor have significant consequences from the synthetic point of view.

The formation of a carbocation-type transition state can account for the inactivity of primary alcohols, such as 1-octanol. Indeed, competitive hydrogenation of 1-octanol and cyclooctanol gave >97% cyclooctanone; 1-octanol was recovered unchanged (Figure 4).

On the contrary, allylic alcohols react very fast, much faster than their saturated analogues, as shown by the comparison between mirtenol and mirtanol (entry 18 versus 19) and of carveol and dihydrocarveol (entry 16 versus 17) although in this last case steric effects may also play a role. Selectivity is not high when secondary reactions can take place, as in the case of geraniol, which under these conditions gives citronellol and isopulegol,[28] but anaerobic conditions avoid formation of the corresponding carboxylic acid which are often observed when using gold catalysts.[12a,29]

The oxidation of carveol requires some more comments. Thus, under catalytic dehydrogenation conditions both nickel and conventional copper-based catalysts convert carveol into carvacrol and tetrahydrocarvone, therefore methods proposed for this transformation on the industrial scale rely on the use of Oppenauer oxidation systems[30,31] or homogeneous dehydrogenation systems.[32] On the contrary, over Cu/Al_2O_3 carveol was oxidized with 88% selectivity under standard conditions and with 95% selectivity by only using two equivalents of hydrogen acceptor, giving carvone, one of the more sought after compounds in the flavor and fragrances industry. On the other hand, in the absence of styrene, dihydrocarvone could be obtained in moderate yield directly from carveol, acting as both the hydrogen donor and acceptor (Scheme 2).

In addition, perillyl aldehyde is typically obtained from perillyl alcohol through Oppenauer-type oxidation systems in the presence of alkylboron compounds and six equivalents of pivalaldehyde[33] or in the presence of aluminium

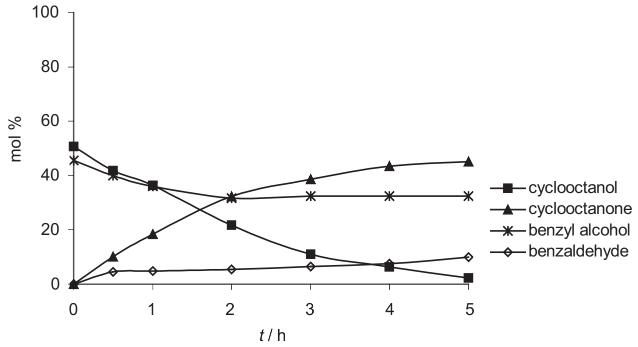


Figure 2. Competitive dehydrogenation of cyclooctanol and benzyl alcohol in the presence of styrene. Reaction conditions: benzyl alcohol (0.5 mmol), cyclooctanol (0.5 mmol), styrene (1 mmol), 8 % Cu/Al_2O_3 (100 mg), toluene (8 mL), 363 K, N_2 atmosphere.

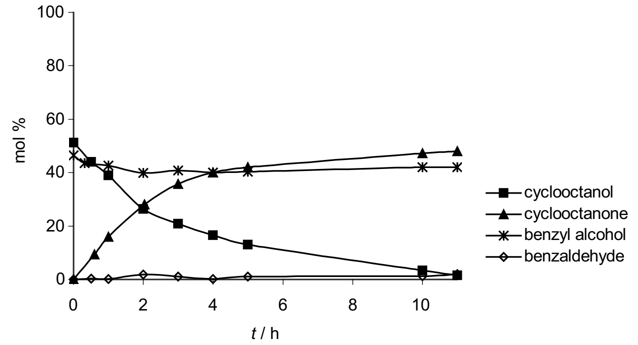


Figure 3. Competitive dehydrogenation of cyclooctanol and benzyl alcohol in the absence of styrene Reaction conditions: benzyl alcohol (0.5 mmol), cyclooctanol (0.5 mmol), 8 % Cu/Al_2O_3 (100 mg), toluene (8 mL), 363 K, N_2 atmosphere.

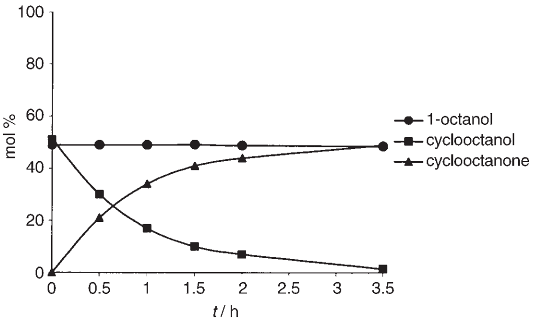
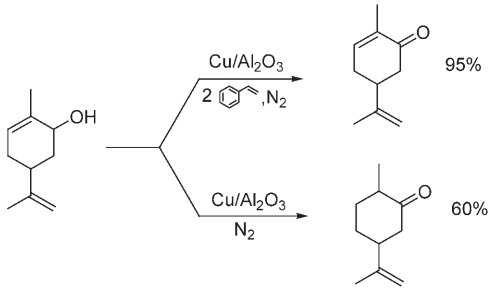


Figure 4. Competitive dehydrogenation of cyclooctanol and 1-octanol. Reaction conditions: 1-octanol (0.5 mmol), cyclooctanol (0.5 mmol), styrene (1 mmol), 8 % Cu/Al_2O_3 (100 mg), toluene (8 mL), 363 K, N_2 atmosphere.

isopropoxide and more than the stoichiometric amounts of nitrobenzaldehyde,[30] whereas under the conditions required by the present system it can be obtained in 86 % yield without formation of any waste but some ethylbenzene (entry 20).

Remarkable activity is observed for nonactivated secondary alcohols that are less easily oxidized by other systems. In particular, a striking activity was observed for cyclohexanol and a series of substituted cyclohexanols (entries 8–12). In the case of 4-*tert*-butylcyclohexanol, for example, the activity based on the total metal content ($TOF = 3.5\ h^{-1}$) is comparable with that observed under aerobic conditions both over 1 % Pd/MgO ($TOF = 3.5\ h^{-1}$)[12b] and 1 % Ru/Al_2O_3 ($TOF = 2.1\ h^{-1}$),[22] whereas for cyclooctanol the activity ($TOF = 12.5\ h^{-1}$) is higher than that observed for both systems ($TOF = 3.2\ h^{-1}$ for Pd/MgO and $TOF = 2.7\ h^{-1}$ for Ru/Al_2O_3). However, if we consider productivity expressed as $g_{product}/g_{catalyst} \times h$, Cu/Al_2O_3 turns out to be one order of magnitude more active than the other two systems for the dehydrogenation of 4-*tert*-butylcyclohexanol and two orders of magnitude for the dehydrogenation of cyclooctanol.



Scheme 2.

The catalyst is efficient for at least six catalytic runs without relevant loss in activity or in selectivity. The Cu content before use and after six runs was found to be unchanged by AAS analysis, while Cu in the filtrates was found to be absent by GF-AAS. Moreover, TPR profiles before and after six runs appeared to be identical, showing the high stability of the metallic phase (Figure 5).

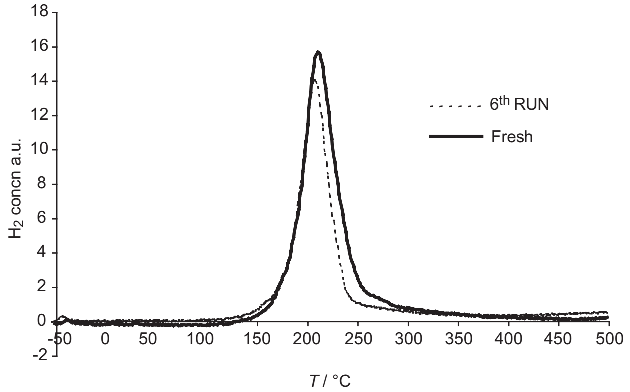


Figure 5. TPR profiles of the fresh catalyst and of the catalyst used for six catalytic runs.

Experimental Section

Cu/Al_2O_3 was prepared as already reported[17] by chemisorption-hydrolysis using alumina from Grace Davison ($BET = 300\ m^2g^{-1}$, pore volume $= 1.0\ mL\,g^{-1}$). The powder was added to a $[Cu(NH_3)_4]^{2+}$ solution prepared by dropping aqueous NH_3 to a $Cu(NO_3)_2{\cdot}3H_2O$ solution until pH 9 had been reached. After 20 min under stirring, the slurry, held in an ice bath at 273 K, was diluted with water. The solid was separated by filtration, washed with water, dried overnight at 383 K, and calcined in air at 673 K for 4 h.

Before reaction, the catalyst (100 mg) was treated in the reaction vessel for 20 min in air at 543 K, for 20 min under reduced pressure, and then reduced in hydrogen (1 atm) at the same temperature.

The substrates (100 mg, 200 mg for steroids) and styrene (1 equiv) were dissolved in toluene (8 mL) and the solution transferred under nitrogen into the reaction vessel containing the prereduced catalyst (100 mg). Catalytic tests were carried out at 363 K under nitrogen and with magnetic stirring (1000 rpm).

For the recycling test, the catalyst was separated by filtration after reaction, washed with acetone, dried, and reactivated by hydrogenation before recycling.

The reaction mixtures were analyzed by means of GC (nonbonded biscyanopropyl-polysiloxane capillary column, 100 m), GCMS (HP-5 MS cross-linked 5% phenyl methyl silicone, 30 m), and ^{1}H NMR (Bruker, 300 MHz) spectroscopy.

Competitive reactions, were carried out by preparing a solution of the two substrates in an equimolar ratio and styrene (2 equiv) in toluene (8 mL).

TPR experiments were conducted on a Micromeritics Pulse Chemisorb 2700 apparatus. Samples were calcined in O_2 flow (50 mL min^{-1}) at 773 K for 1 h, cooled down to 200 K in Ar flow (50 mL min^{-1}), and then TPR was performed in H_2 (8%)/Ar flow (15 mL min^{-1}, heating rate 8° min^{-1} to 773 K).

The copper content analyses of the solutions were performed by graphite furnace atomic absorption spectroscopy (GF-AAS) by using a GBC 908 AA instrument and the analysis of the catalysts by a Perkin–Elmer 400 atomic absorption spectrophotometer.

Conclusion

The Cu/Al_2O_3-catalyzed transfer dehydrogenation reaction has been shown to be a versatile and powerful tool for the oxidation of secondary and allylic alcohols under very mild conditions. Electronic effects and the choice of the acceptor make this catalytic system unique as it allows selective oxidation of a secondary alcohol in the presence of an unprotected primary alcohol and also of a benzylic alcohol. Moreover, the catalyst can also be used for hydrogenation and cyclization reactions, always showing excellent selectivity, good productivity, stability, and reusability, basic features for the application of heterogeneous catalysts to fine-chemical synthesis.

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[1] J. C. Collins, W. W. Hess, F. J. Frank, *Tetrahedron Lett.* **1968**, *9*, 3363–3366.
[2] K. E. Harding, L. M. May, K. F. Dick, *J. Org. Chem.* **1975**, *40*, 1664–1665.
[3] E. J. Corey, J. W. Suggs, *Tetrahedron Lett.* **1975**, *16*, 2647–2650.
[4] E. J. Corey, G. Schmidt, *Tetrahedron Lett.* **1979**, *20*, 399–402.
[5] A. J. Mancuso, D. Swern, *Synthesis* **1981**, 165–185.
[6] S. V. Ley, J. Norman, W. P. Griffith, S. P. Marsden, *Synthesis* **1994**, 639–666.
[7] M. Gilhespy, M. Lok, X. Baucherel, *Chem. Commun.* **2005**, 1085–1086.
[8] G. Pozzi, M. Cavazzini, S. Quici, M. Tenaglia, G. Dell'Anna, *Org. Lett.* **2004**, *6*, 441–443.
[9] R. A. Sheldon, I. W. C. E. Arends, *Adv. Synth. Catal.* **2004**, *346*, 1051–1071.
[10] H. Tohma, Y. Kita, *Adv. Synth. Catal.* **2004**, *346*, 111–124.
[11] a) I. E. Markò, A. Gautier, R. Dumeunier, K. Doda, S. Philippart, S. M. Brown, C. J. Urch, *Angew. Chem.* **2004**, *116*, 1614–1617; *Angew. Chem. Int. Ed.* **2004**, *43*, 1588–1591, and references therein; b) P. Gamez, I. W. C. E. Arends, R. A. Sheldon, J. Reedijk, *Adv. Synth. Catal.* **2004**, *346*, 805–811.
[12] a) A. Abad, P. Conception, A. Corma, H. Garcia, *Angew. Chem.* **2005**, *117*, 4134–4137; *Angew. Chem. Int. Ed.* **2005**, *44*, 4066–4069; b) U. R. Pillai, E. Sahle-Demessie, *Green Chem.* **2004**, *6*, 161–165; c) for a review see T. Mallat, A. Baiker, *Chem. Rev.* **2004**, *104*, 3037–3058.
[13] M. Hayashi, K. Yamada, S. Nakayama, H. Hayashi, S. Yamazaki, *Green Chem.* **2000**, *2*, 257–260.
[14] T. Tanaka, H. Kawabata, M. Hayashi, *Tetrahedron Lett.* **2005**, *46*, 4989–4991.
[15] C. Keresszegi, T. Mallat, A. Baiker, *New J. Chem.* **2001**, *25*, 1163–1167.
[16] R. Karvembu, R. Prabhakaran, K. Senthilkumar, P. Viswanathamurty, K. Natarajan, *React. Kinet. Catal. Lett.* **2005**, *86*, 211–216.
[17] F. Zaccheria, N. Ravasio, A. Fusi, R. Psaro, *Chem. Commun.* **2005**, 253–255.
[18] F. Zaccheria, A. Fusi, R. Psaro, N. Ravasio in *Catalysis of Organic Reactions, Chem. Industry, Vol. 104* (Ed.: J. R. Sowa Jr.), Taylor & Francis, Boca Raton, **2005**, pp. 293–301.
[19] N. Ravasio, F. Zaccheria, A. Fusi, R. Psaro, *Recent. Res. Devel. Catalysis* **2005**, *3*, 1–15.
[20] N. Ravasio, M. Antenori, M. Gargano, P. Mastrorilli, *Tetrahedron Lett.* **1996**, *37*, 3529–3532.
[21] N. Ravasio, F. Zaccheria, M. Guidotti, R. Psaro, *Top. Catal.* **2004**, *27*, 157–168.
[22] a) K. Yamaguchi, N. Mizuno, *Angew. Chem.* **2002**, *114*, 4720–4724; *Angew. Chem. Int. Ed.* **2002**, *41*, 4538–4542; b) K. Yamaguchi, N. Mizuno, *Chem. Eur. J.* **2003**, *9*, 4353–4361.
[23] U. K. Singh, M. N. Sysak, M. A. Vannice, *J. Catal.* **2000**, *191*, 181–191.
[24] F. Zaccheria, N. Ravasio, A. Fusi, R. Psaro, *Tetrahedron Lett.* **2005**, *46*, 3695–3697.
[25] R. M. Rioux, M. A. Vannice, *J. Catal.* **2003**, *216*, 362–376.
[26] V. Z. Fridman, A. A. Davydov, K. Titiesky, *J. Catal.* **2004**, *222*, 545–557.
[27] V. Z. Fridman, A. A. Davydov, *J. Catal.* **2000**, *195*, 20–30.
[28] F. Zaccheria, N. Ravasio, A. Fusi, M. Rodondi, R. Psaro, *Adv. Synth. Catal.* **2005**, *347*, 1267–1272.
[29] D. I. Enache, D. W. Knight, G. J. Hutchings, *Catal. Lett.* **2005**, *103*, 43–52.
[30] S. Tanikawa, S. Matsubayashi, M. Tanikawa, T. Komatsu (Nikken Chem. Ltd., Japan) US-Pat. Appl. 2002198411, **2002** [*Chem. Abstr.* **2003**, *138*, 39431j].
[31] T. Ooi, H. Otsuka, T. Miura, H. Ichikawa, K. Maruoka, *Org. Lett.* **2002**, *4*, 2669–2672.
[32] G. Kolomeyer, J. S. Oyloe (Millenium Speciality Chem. USA), PCT Int. Appl. WO 2004108646, **2004** [*Chem. Abstr.* **2005**, *142*, 56539a].
[33] K. Ishihara, H. Kurihara, H. Yamamoto, *J. Org. Chem.* **1997**, *62*, 5664–5665.

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