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Allylic oxidation of olefins in the presence of Cu-Na-HSZ-320 zeolite as reusable solid catalyst

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Abstract

The Cu-Na-HSZ-320 zeolite can be utilised as an efficient and reusable catalyst in the allylic oxidation of olefins with *tert*-butyl perbenzoate to give the corresponding allylic esters in good yield and excellent selectivity. © 2000 Elsevier Science Ltd. All rights reserved.

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The allylic oxidation of olefins is recognised as one of the most useful routes to produce allylic alcohols, esters and ethers.[1] In particular, oxidation of C–H bonds by copper catalysed reaction with an organic peroxyester (the Kharasch–Sosnovsky reaction) represents an easy and general methodology for the synthesis of esters of allylic alcohols.[2] Moreover, considerable attention has been devoted recently to the asymmetric Kharasch–Sosnovsky reaction in the presence of chiral copper complexes.[3]

Recent years have seen an increasing interest into the catalysis by solid materials for fine chemicals preparation[4] since this approach frequently results in an improvement of the productive process from both an economical and ecological point of view.[5]

Our interest in the preparation and use of solid catalysts for the production of fine chemicals[6] prompted us to reinvestigate the Kharasch–Sosnovsky reaction over copper-exchanged zeolites.

The catalysts utilised were Cu-Na-HSZ-320 and Cu-Na-ZSM-5 prepared by a conventional ion-exchange method[7] in which commercially available zeolites Na-HSZ-320[8] or H-ZSM-5[9] were treated with an aqueous solution of Cu(II) nitrate at 90°C for 2 hours, washed with deionised water, filtered, dried and calcined at 500°C for 15 hours in air.[10] Although the effective catalyst in the Kharasch–Sosnovsky reaction has been suggested to be a Cu(I) species,[11] we decided to use Cu(II)-exchanged zeolites on the basis of recent results from literature[12] and previous

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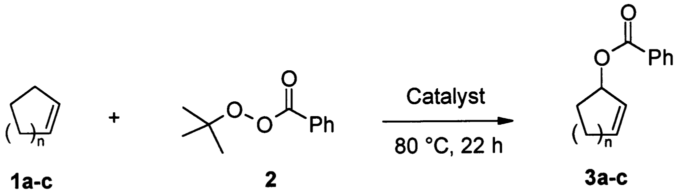
experience from our laboratory suggesting that both Cu(I)- and Cu(II)-exchanged Na-HSZ-320 zeolites showed similar catalytic efficiency.

A first series of experiments was performed by reacting *tert*-butylperbenzoate **2** with various cycloalkenes **1a**–**c** in the presence of the two Cu(II)-exchanged zeolites with different pore dimensions. Results reported in Table 1 suggest that despite the quite similar copper content the two zeolites show a dramatically different catalytic efficiency.

Table 1
Allylic oxidation of cycloalkenes using two different Cu(II)-exchanged zeolites[a]



Entry	*n*	**3** Yield (%)	
		Cu-Na-HSZ-320 [Cu (% wt): 2.8]	Cu-Na-ZSM-5 [Cu (% wt): 2.0]
a	1[b]	60	7
b	2	70	4
c	4	68	5

[a] **1a**–**c** (0.030 mol), **2** (0.010 mol), cat. (0.1 g).

[b] Reaction temperature = 45°C (cyclopentene bp = 44°C).

These results can be rationalised assuming that the diffusion of reagents and products through the zeolite Cu-Na-HSZ-320 (pore dimension 7.4 Å) is almost completely unrestricted whereas Cu-Na-ZSM-5 (pore dimension 5.1–5.6 Å) can suffer from some diffusion resistance which hampers the accessibility to the surface active sites of the catalyst.

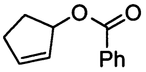
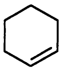
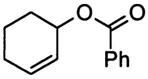
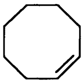
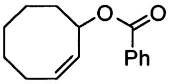
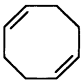
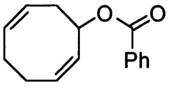
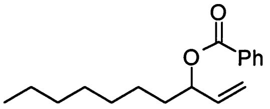
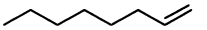
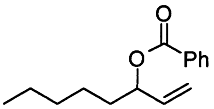
The reaction with the zeolite Cu-Na-HSZ-320 can be successfully applied to different olefins giving allylic benzoates in satisfactory to good yields[13] (Table 2).

The mildness of the reaction conditions makes it possible to use both cyclic and linear olefins giving the corresponding allylic benzoates without formation of any side products such as isomeric compounds obtained by allylic rearrangement frequently observed when the reaction is carried out under homogeneous catalysis.[14]

The possible leaching of copper catalyst was then examined by using the standard procedure suggested by R. A. Sheldon.[15] Thus, the model reaction mixture between **1b** and **2** in the presence of Cu-Na-HSZ-320 was filtered at 80°C after 10 hours when **3b** was produced in 44% yield. An additional amount of reagents **1b** (30 mmol, 2.5 g, 3.0 ml) and **2** (10 mmol, 1.6 g, 1.9 ml) was added to the solution and the solid catalyst, and both reaction mixtures were heated at 80°C for a further 10 hours. Production of **3b** in 42% yield with the solid catalyst and in about 3% yield with the solution confirms that the reaction mainly occurs on the surface of the solid catalyst.

Finally, the zeolite Cu-Na-HSZ-320 has been recycled almost 10 times in the model reaction between **1b** and **2** showing a modest increase in efficiency: from 70% in the first cycle to 79% in the last cycle.

Table 2
Synthesis of various allylic benzoates **3** promoted by Cu-Na-HSZ-320 zeolite

Entry	Olefin **1**	Product **3**	Yield [Selectivity] (%)
a			60 [97]
b			70 [99]
c			68 [95]
d			82 [98]
e			32 [97]
f			38 [96]

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References

1. Bulman Page, P. C.; McCarthy, T. J. In *Comprehensive Organic Synthesis*; Trost, B. M.; Fleming, J.; Heathcock, C. H., Eds.; Pergamon: Oxford, 1991; Vol. 7, Chapter 2.1, pp. 83–117.
2. (a) Kharasch, M. S.; Sosnovsky, G. *J. Am. Chem. Soc.* **1958**, *80*, 756; (b) Kharasch, M. S.; Sosnovsky, G.; Yang, N. C. *J. Am. Chem. Soc.* **1959**, *81*, 5819; (c) Sosnovsky, G.; Yang, N. C. *J. Org. Chem.* **1960**, *25*, 899; (d) Sosnovsky, G. *Tetrahedron* **1961**, *13*, 241; (e) Sosnovsky, G.; O'Neill, H. J. *C. R. Hebd. Seances Acad. Sci.* **1962**, *254*, 704; (f) Sosnovsky, G.; Rawlinson, D. J. In *Organic Peroxides*; Swern, D., Ed.; Wiley: New York, 1970; Vol. 1; (g) Rawlinson, J.; Sosnovsky, G. *Synthesis* **1972**, 1.

3. (a) Ievina, A.; Muzart, J. *Tetrahedron: Asymmetry* **1995**, *6*, 147; (b) Muzart, J. *J. Mol. Catal.* **1991**, *64*, 381; (c) Andrus, M. B.; Chen, X. *Tetrahedron* **1997**, *53*, 16229; (d) Södergren, M. J.; Andersson, P. G. *Tetrahedron Lett.* **1996**, *37*, 7577; (e) Zorrdervan, C.; Feringa, B. L. *Tetrahedron: Asymmetry* **1996**, *7*, 1895; (f) Kawasaki, K.; Katsuki, T. *Tetrahedron* **1997**, *53*, 6337; (g) Andrus, M. B.; Argade, A. B.; Chen, X.; Pammnet, M. G. *Tetrahedron Lett.* **1995**, *36*, 2945.
4. (a) Hutchings, G. J. *J. Chem. Soc., Chem. Commun.* **1999**, 301; (b) Corma, A. *Chem. Rev.* **1995**, *95*, 559; Balogh, M.; Laszlo, P. *Organic Chemistry Using Clays*; Springer Verlag: New York, 1993.
5. (a) Clark, J. H.; Macquarrie, D. J. *Chem. Soc. Rev.* **1996**, 303; (b) Sheldon, R. A. *Chem. Ind. (London)* **1997**, 12; (c) Sheldon, R. A. *J. Mol. Catal. A.* **1996**, *107*, 75; Thomas, J. M.; Zamaraev, K. I. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 308.
6. (a) Bigi, F.; Maggi, R.; Sartori, G.; Zambonin, E. *J. Chem. Soc., Chem. Commun.* **1998**, 513; (b) Bigi, F.; Frullanti, B.; Maggi, R.; Sartori, G.; Zambonin, E. *J. Org. Chem.* **1999**, *64*, 1004; (c) Ballabeni, M.; Ballini, R.; Bigi, F.; Maggi, R.; Parrini, M.; Predieri, G.; Sartori, G. *J. Org. Chem.* **1999**, *64*, 1029.
7. Hayashibara, H.; Nishiyama, S.; Tsuruya, S.; Masai, M. *J. Catal.* **1995**, *153*, 254.
8. Na-HSZ-320 is an FAU zeolite with 5.6 SiO_2/Al_2O_3 molar ratio, pore size 7.4 Å and surface area 570±10 m^2/g.
9. H-ZSM-5 is an MFI zeolite with 28.2 SiO_2/Al_2O_3 molar ratio, pore size 5.1–5.6 Å and surface area 410±10 m^2/g It was converted into Na-ZMS-5 according to Ref. 7.
10. Herron, N. *Inorg. Chem.* **1986**, *25*, 4714. The Cu content (% weight) in the Cu-Na-HSZ-320 and Cu-Na-ZSM-5 was 2.8 and 2.0, respectively (determined by AAS).
11. Sosnovsky, G. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 269.
12. Sekar, G.; Datta Gupta, A.; Singh, V. K. *Tetrahedron Lett.* **1996**, *37*, 8435.
13. The general procedure for the preparation of allyl benzoates **3** is as follows: a mixture of the selected alkene **1** (30 mmol) and Cu-Na-HSZ-320 (0.1 g) was heated at 80°C and then *tert*-butylperbenzoate **2** (10 mmol, 1.9 g, 1.9 ml) was added dropwise over a 20 hour period. After an additional 2 hours, the mixture was cooled to rt, the catalyst was removed by filtration, washed with methylene chloride (40 ml) and acetone (20 ml) and the crude was treated with a saturated solution of $NaHCO_3$ (2×25 ml) and water (2×25 ml). The organic phase was dried ($NaSO_4$), the excess olefin was recovered unchanged by distillation and the products purified by flash chromatography using a mixture of hexane/ethyl acetate 95/5 as eluant. All products **3a**–**f** were characterised (IR, ^{1}H NMR and MS) and their bps compared with reported literature bps. Physical data of **3d**: pale yellow oil, bp 135–140°C/0.1 mmHg; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 1.5$–1.3 (m, 6H, $3CH_2$), 5.4–5.8 (m, 4H, H-2, H-3, H-6 and H-7), 6.1–6.3 (m, 1H, H-1), 7.40 (t, 2H, $J = 7.6$, H-3′ and H-5′), 7.51 (tm, 1H, $J = 7.6$, H-4′), 8.05 (dm, 2H, $J = 7.6$, H-2′ and H-6′); IR (NaCl): 1717 cm^{-1}; MS (CI): m/z 228 (M^+, 3%), 105 (100), 77 (49); Anal. calcd for $C_{15}H_{16}O_2$: C, 78.9, H, 7.1; found: C, 79.1, H, 7.3. Physical data of **3e**: pale yellow oil, bp 124–128°C/0.1 mmHg; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 0.87$ (t, 3H, $J = 7.0$, CH_3), 1.1–1.9 (m, 12H, $6CH_2$), 5.20 (dt, 1H, $J = 10.5$ and 1.2, H-1_{trans}), 5.32 (dt, 1H, $J = 17.1$ and 1.2, H-1_{cis}), 5.49 (qm, 1H, $J = 6.4$, H-3), 5.90 (ddd, 1H, $J = 17.1$, 10.5 and 6.4, H-2), 7.44 (tm, 2H, $J = 7.5$, H-3′ and H-5′), 7.55 (tt, 1H, $J = 7.5$ and 1.4, H-4′), 8.06 (dm, 2H, $J = 7.5$, H-2′ and H-6′); IR (NaCl): 1718 cm^{-1}; MS (CI): m/z 260 (M^+, 3%), 105 (100), 77 (23); Anal. calcd for $C_{17}H_{24}O_2$: C, 78.4, H, 9.3; found: C, 78.2, H, 9.2.
14. See for example: (a) Kochi, J. K. *J. Am. Chem. Soc.* **1961**, *83*, 3162; (b) Denney, D. Z.; Appelbaum, A.; Denney, C. B. *J. Am. Chem. Soc.* **1962**, *84*, 4969; (c) Kochi, J. K. *J. Am. Chem. Soc.* **1962**, *84*, 774; (d) Walling, C.; Zavitsas, A. A. *J. Am. Chem. Soc.* **1963**, *85*, 2084; (e) Rawlinson, J.; Sosnovsky, G. *Synthesis* **1972**, 567.
15. Lempers, H. E. B.; Sheldon, R. A. *J. Catal.* **1998**, *175*, 62.