Mn^{2+}-Exchanged Clay-catalysed Oxidation of Alkanes with *tert*-Butyl Hydroperoxide

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Oxidation of alkanes such as cyclohexane, cyclooctane, adamantane and octane with 70% aqueous *tert*-butyl hydroperoxide in benzene in the presence of Mn^{2+}-exchanged clay catalyst and molecular sieves 4 Å produces mainly the corresponding ketones with high turnover numbers.

Transition metal-catalysed oxidation of alkanes under mild conditions is one of the important targets of recent chemistry and many reports have appeared.[1] However, only a few attempts have been made on the alkane oxidation by use of solid supports. Thus, manganese(III) porphyrins adsorbed on several solid supports such as Na$^+$–montmorillonite (Na$^+$–mont), Al_2O_3 and SiO_2 were used for alkane hydroxylation at 20 °C with PhIO.[2] Another example was a patent work of air oxidation of cyclohexane to cyclohexanone and cyclohexanol in the presence of Co^{3+}–philosilicate at 125 °C.[3] We are currently interested in the use of a variety of clays for organic synthesis,[4,5] and now find that Mn^{2+}–mont and/or freshly prepared Mn^{2+}–fluorotetrasilicic mica (Mn^{2+}–TSM)† work as efficient catalysts for alkane oxidation with commercially available 70% aqueous *tert*-butyl hydroperoxide (TBHP).

Treatment of cyclohexane **1** with 70% aqueous TBHP in benzene at 60 °C for 48 h in the presence of Mn^{2+}–TSM afforded cyclohexanone **2** (major) and cyclohexanol **3** (minor) in 7.3% yield, while Mn^{2+}–mont did not show any reactivity as a catalyst. The reaction did not proceed at all at 25 °C. When molecular sieves 4 Å (MS 4 Å) were added to the reaction system the product yields increased and, interestingly, even Mn^{2+}–mont became active. It may act as a dehydrating agent keeping the system dry and the catalyst active. The amount of cations on Mn^{2+}–mont and Mn^{2+}–TSM was estimated by X-ray fluorescence (XRF) analysis to be 0.300 and 0.115 mmol g^{-1}, respectively, and the turnover numbers were calculated based on the amount of cations. Other M^{n+}–mont such as Al^{3+}–, Fe^{3+}–, Ce^{3+}–, H$^+$– and Na$^+$–mont showed only a very low catalytic activity for the oxidation of **1** even in the presence of MS 4 Å. For comparison, the oxidation was also carried out in the presence of MnO_2 which showed a catalytic activity similar to Mn^{2+}–mont if MS 4 Å present.

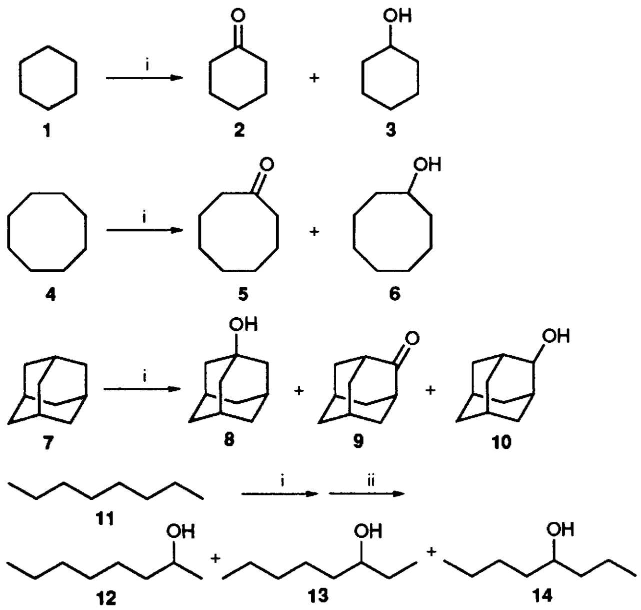
Since a combination of Mn^{2+}–TSM with MS 4 Å showed a highest reactivity for oxidation of **1**, this system was applied to other alkanes such as cyclooctane **4**, adamantane **7** and octane **11**.‡ Typical results are shown in Table 1 together with the results of the corresponding control experiments. All results were reproducible and Mn^{2+}–TSM was revealed to be a very efficient catalyst except the case of an unreactive **11**. From **4** and **7**, cyclooctanone and adamantan-1-ol were the main products, respectively. From **11**, there is no evidence for octanal formation. The main products from **11** were ketones which were reduced with lithium aluminium hydride to alcohols for convenience of GLC determination. These results indicate that the reactivity order is tertiary C–H > secondary C–H > primary C–H, and the alkane reactivity is in the decreasing order of adamantane > cyclooctane > cyclohexane > octane considering both the turnover numbers and the product yields. The initial product seems to be an alcohol, as shown by the favourable formation of **8** from **7**, which is then oxidised to the corresponding ketone as we confirmed separately.

We wish to thank Kunimine Industries Co., Ltd. for the gift

Table 1 Catalytic oxidation of alkanes with 70% aqueous TBHP[a]

Run	Alkane	Catalyst (mmol)[b]	MS 4 Å (g)	Products GLC yield (%)[c]			Turnover number[d]
				2		**3**	
1	**1**	Mn^{2+}–TSM (0.012)	0	6.2		1.1	61
2	**1**	Mn^{2+}–TSM (0.012)	0.50	8.5		0.8	78
3	**1**	Mn^{2+}–TSM (0.012)	1.00	11.2		2.2	112
4	**1**	Mn^{2+}–mont (0.012)	0	0.3		0.5	7
5	**1**	Mn^{2+}–mont (0.012)	1.00	7.9		1.1	75
6	**1**	Na$^+$–mont (0.117)	0	0.1		0.1	0
7	**1**	—	0	0.4		0.3	—
8	**1**	—	1.00	0.1		0.2	—
9	**1**	MnO_2 (0.012)	0	0.7		0.5	10
10	**1**	MnO_2 (0.012)	1.00	7.5		1.9	78
				5		**6**	
11	**4**	Mn^{2+}–TSM (0.012)	1.00	21.2		3.7	208
12	**4**	Mn^{2+}–mont (0.012)	1.00	17.5		3.0	171
13	**4**	—	1.00	1.2		0.9	—
14	**4**	MnO_2 (0.012)	1.00	5.6		1.9	63
				8	**9**	**10**	
15	**7**	Mn^{2+}–TSM (0.012)	1.00	26.1	12.7	0.7	329
16	**7**	Mn^{2+}–mont (0.012)	1.00	27.6	7.7	0.3	297
17	**7**	—	1.00	1.3	0.5	<0.1	—
18	**7**	MnO_2 (0.012)	1.00	8.7	2.5	0.2	95
				12	**13**	**14**	
19	**11**	Mn^{2+}–TSM (0.012)	1.00	2.9	2.0	1.9	57
20	**11**	Mn^{2+}–mont (0.012)	1.00	3.2	2.1	2.0	61
21	**11**	—	1.00	1.5	1.0	1.0	—
22	**11**	MnO_2 (0.012)	1.00	4.1	2.7	2.6	78

[a] *Reaction conditions*: alkane (10.0 mmol), 70% aqueous TBHP (45.0 mmol), catalyst, additive, benzene (4 cm^3) at 60 °C for 48 h. [b] Of cations. [c] Based on cyclohexane. [d] Based on the amount of cations.



Scheme 1 *Reagents and conditions*: i, 70% aqueous TBHP, catalyst, additive, benzene at 60 °C for 48 h; ii, $LiAlH_4$, diethyl ether, room temp.

of Kunipia G. We also thank Topy Industries Co., Ltd. for the gift of Na^+–TSM.

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Footnotes

† Mn^{2+}–mont (a pale yellow-brown or beige coloured solid) was prepared by treatment of Na^+–mont (commercially available, Kunimine Industries Co., Ltd.) by stirring with $Mn(NO_3)_2{\cdot}6H_2O$ in aqueous acetone at 50 °C for 24 h, by collecting by filtration and by washing with pure water as described previously.[4a] Mn^{2+}–TSM (a pale yellow-brown or beige coloured solid) was similarly prepared by treatment of Na^+–TSM (commercially available, Topy Industries Co., Ltd.) with $Mn(NO_3)_2{\cdot}6H_2O$ in aqueous acetone.[6] The basal spacings (d_{001}) of Mn^{2+}–mont and Mn^{2+}–TSM were estimated by a sharp peak obtained on X-ray powder diffraction (XRD) analysis to be 14.9 and 14.3 Å, respectively, showing clearly that the catalysts have an interlayer structure.

‡ A typical experimental procedure is as follows. To a mixture of adamantane **7** (1.36 g, 10.0 mmol), benzene (4 cm^3) and commercially available 70% aqueous TBHP (5.79 g, 45.0 mmol) were added Mn^{2+}–TSM (100 mg, 0.012 mmol as Mn^{2+}) and MS 4 Å (1.00 g, powder) with one portion at 25 °C with magnetic stirring. The mixture was then stirred at 60 °C for 48 h. After cooling, the catalyst and MS 4 Å were collected by filtration and washed with diethyl ether (20 cm^3). The products in the combined filtrate and washings were determined by GLC analysis with acetophenone as an internal standard; adamantan-1-ol (397.7 mg, 2.61 mmol, 26.1%), adamantan-2-one (191.1 mg, 1.27 mmol, 12.7%) and adamantan-2-ol (10.9 mg, 0.07 mmol, 0.7%): total yield 39.5%, turnover number 329.

References

1 For examples, R. H. Crabtree and A. Habib, *Comprehensive Organic Synthesis*, ed. B. M. Trost, I. Fleming and S. V. Ley, Pergamon Press, Oxford, 1991, vol. 7, ch. 1.1.11, pp. 10–14; K. Nomura and S. Uemura, *J. Chem. Soc., Chem. Commun.*, 1994, 129; G. K. Cook and J. M. Mayer, *J. Am. Chem. Soc.*, 1994, **116**, 1855.
2 L. Barloy, J. P. Lallier, P. Battioni, D. Mansuy, Y. Piffard, M. Tournoux, J. B. Valim and W. Jones, *New. J. Chem.*, 1992, **16**, 71.
3 K. Hashimoto, Y. Asahi and T. Maki, *Jap. Pat.* 88 303 936, 1988; *Chem. Abstr.*, 1989, **111**, 6957z.
4 (*a*) J. Tateiwa, H. Horiuchi, K. Hashimoto, T. Yamauchi and S. Uemura, *J. Org. Chem.*, in the press; (*b*) J. Tateiwa, H. Horiuchi and S. Uemura, *Bull. Chem. Soc. Jpn.*, in the press.
5 For recent reviews on the reactions in the presence of clays, see: M. Balogh and P. Laszlo, *Organic Chemistry Using Clays*, Springer-Verlag, New York, 1993; F. J. A. Kellendonk, J. J. L. Heinerman, R. A. van Santen, A. McKillop, D. W. Clissold, T. J. Pinnavaia, A. Foucaud and J. M. Adams, *Preparative Chemistry Using Supported Reagents*, ed. P. Laszlo, Academic Press, New York, 1987, part 8, pp. 453–528.
6 Y. Monikawa, T. Goto, Y. Mono-oka and T. Ikawa, *Chem. Lett.*, 1982, 1667.