

Mn²⁺-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 Mn²⁺-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), Al₂O₃ and SiO₂ 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 Co³⁺-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 Mn²⁺-mont and/or freshly prepared Mn²⁺-fluorotetrasilic mica (Mn²⁺-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 Mn²⁺-TSM afforded cyclohexanone **2** (major) and cyclohexanol **3** (minor) in 7.3% yield, while Mn²⁺-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 Mn²⁺-mont became active. It may act as a dehydrating agent keeping the system dry and the catalyst active. The amount of cations on Mn²⁺-mont and Mn²⁺-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 Mⁿ⁺-mont such as Al³⁺-, Fe³⁺-, Ce³⁺-, 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 MnO₂ which showed a catalytic activity similar to Mn²⁺-mont if MS 4 Å present.

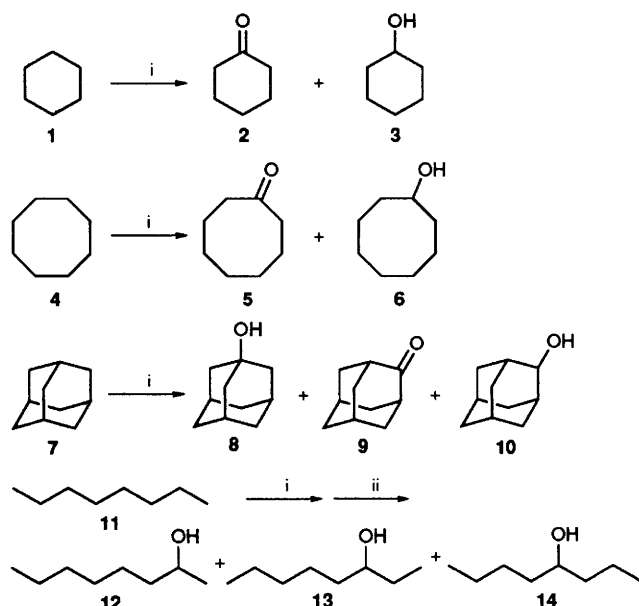
Since a combination of Mn²⁺-TSM with MS 4 Å showed a highest reactivity for oxidation of **1**, this system was applied to other alkanes such as cyclooctane **4**, adamantane **7** and octane **11**.[‡] Typical results are shown in Table 1 together with the results of the corresponding control experiments. All results were reproducible and Mn²⁺-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 cm³) 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.

Received, 1st August 1994; Com. 4/04693E

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 $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 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 $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 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 cm³) 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 cm³). 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.

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