Cation-exchanged fluorotetrasilicic mica (M^{n+}–TSM; M^{n+} = Mn^{2+}, Cr^{3+}, Co^{2+} and Cu^{2+})-catalysed oxidation of alkanes with *tert*-butyl hydroperoxide

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Oxidation of alkanes such as cyclohexane **1**, cyclooctane **4**, cyclododecane **7**, adamantane **10**, octane **14**, methylcyclohexane **18** and 2,5-dimethylhexane **23** with 70% aqueous *tert*-butyl hydroperoxide has been investigated in benzene in the presence of cation-exchanged fluorotetrasilicic mica (M^{n+}–TSM; M^{n+} = Mn^{2+}, Cr^{3+}, Co^{2+} and Cu^{2+}) and molecular sieves 4 Å. Compound **1** was oxidised to cyclohexanone **2** (a major product) and cyclohexanol **3** in 9.7–13.4% GLC yield with turnover numbers 154–205, where Mn^{2+}–TSM gave the highest turnover number. Similarly, other alkanes **4**, **7**, **10**, **14**, **18** and **23** were oxidised mainly to the corresponding ketones in the presence of Mn^{2+}–TSM with a turnover number up to 435. It was confirmed in the cyclohexane oxidation that Mn^{2+}–TSM was regenerated and reused. Compounds **1**, **4** and **10** were shape-selectively oxidised in the presence of Cr^{3+}–TSM.

Transition metal-catalysed oxidation of alkanes under mild conditions is one of the important targets of recent chemistry and many reports have appeared.[1] In recent times, a great interest has been taken especially in the use of zeolite and other solid supports in selective alkane oxidation.[2] We are currently interested in the catalytic use of cation-exchanged clays for organic synthesis.[3] These catalysts have advantages such as the ease of handling, non-corrosiveness, low cost, regeneration and ready modification of catalytic activity by cation-exchange in the interlayer space.[4] As one of our series of studies on clay-catalysed organic synthesis we report here the results of our attempts at alkane oxidation. Namely, various transition metal cation-exchanged fluorotetrasilicic micas (M^{n+}–TSM), especially that of manganese (Mn^{2+}–TSM), worked as efficient catalysts for alkane oxidation of a wide range of substrates with commercially available 70% aqueous *tert*-butyl hydroperoxide (TBHP) to give mainly the corresponding ketones.[5]

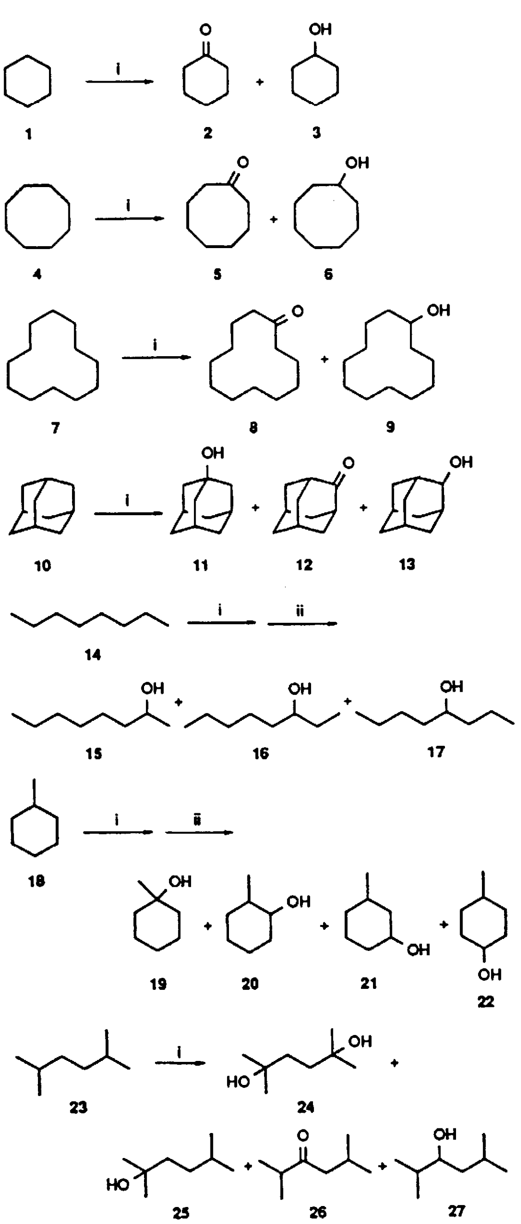
Results and discussion

Oxidation of alkanes with 70% aqueous 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 a mixture of cyclohexanone **2** (major) and cyclohexanol **3** (minor) in 7.3% GLC yield (Scheme 1; Table 1, run 1), while Mn^{2+}-exchanged montmorillonite (Mn^{2+}–mont) did not show any reactivity as a catalyst (Table 1, run 8). 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 yield increased (Table 1, runs 5–7) and, interestingly, even Mn^{2+}–mont became active (Table 1, run 9). It may work as a dehydrating agent to keep the system dry and the catalyst active. The amount of cations on clay catalysts was estimated by X-ray fluorescence (XRF) analysis and the turnover numbers were calculated based on the amount of cations (see Experimental section). Mn^{2+}–TSM had the advantage of being recycled in this oxidation (Table 1, runs 2–4). If the recovered catalyst was washed with acetone and dried, it showed a constant catalytic activity for at least three cycles. For comparison, the oxidation was also carried out in the presence of freshly prepared active MnO_2[6] which showed a catalytic activity similar to Mn^{2+}–mont if MS 4 Å was present (Table 1, runs 12 and 13). On the other hand, commercially available MnO_2 did not show any reactivity as a catalyst even in the presence of MS 4 Å. The product yield depended very much on the nature of M^{n+}–TSM and the best yield was obtained in the reaction catalysed by Mn^{2+}–TSM (Table 1, run 7). Other M^{n+}–TSMs, *e.g.* Cr^{3+}–, Co^{2+}– and Cu^{2+}–TSM, also showed moderate catalytic activity for the oxidation of **1** (Table 1, runs 16–18). In particular, Cr^{3+}–TSM provided **2** selectively. Na^{+}–TSM and other M^{n+}–monts, *e.g.* Fe^{3+}–, Al^{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.

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**, cyclododecane **7**, adamantane **10** and octane **14**. Typical results are also shown in Table 1 together with the results of the corresponding control experiments. All the results were reproducible and Mn^{2+}–TSM was revealed to be a very efficient catalyst except in the case of **14**. The main products from **4**, **7** and **10** were cyclooctanone **5**, cyclododecanone **8** and adamantan-1-ol **11**, respectively (Table 1, runs 19, 24 and 28). There was no evidence for octanal formation from **14**. The main products from **14** were ketones which were reduced with lithium aluminium hydride (LAH) to alcohols for convenience of GLC determination. By considering the product yields the results indicate that the reactivity order is tertiary C–H > secondary C–H ≫ primary C–H. Compared with active MnO_2, Mn^{2+}–TSM is more substrate-selective probably due to its layer structure. The initial product is an alcohol, as shown by the favourable formation of **11** from **10**, which is then oxidised to the corresponding ketone as we confirmed separately (see Experimental section). From the results of oxidation using other M^{n+}–TSM, it was shown that Cr^{3+}–TSM is more shape-selective than Mn^{2+}–TSM. Thus, in the presence of Cr^{3+}–TSM, **4** was oxidised with a turnover number of 608, while **10** was oxidised with a turnover number of 38 (Table 1, runs 23 and 32). Although the details are not yet clear, this tendency might reflect the difference of the layer structures of both M^{n+}–TSM.

Methylcyclohexane **18** and 2,5-dimethylhexane **23**, both of which possess primary, secondary and tertiary C–H bonds in the molecule, were chosen as suitable substrates to evaluate the selectivity of this oxidation (Table 1, runs 40 and 41). The



Scheme 1 *Reagents and conditions:* i, 70% aqueous TBHP, Mn^{2+}–TSM, MS 4 Å, benzene at 60 °C for 48 h; ii, LAH, diethyl ether at room temperature for 24 h

results indicated the same trend to the results obtained from **10** and **14**. Namely, the main products from **18** and **23** were 1-methylcyclohexan-1-ol **19** and 2,5-dimethylhexane-2,5-diol **24**, respectively, both of which were produced by oxidation of tertiary C–H bonds. Any products due to the oxidation of primary C–H bonds were not detected by GLC.

The time course of the cyclohexane oxidation is shown in Fig. 1. The addition of 2-*tert*-butyl-6-methylphenol as a radical scavenger did not have a large effect on the cyclohexane oxidation, which suggests that the oxidation catalysed by M^{n+}–TSM proceeds mainly *via* an ionic pathway. It is well known that alkylphenols scavenge alkylperoxyl radicals and interrupt the autoxidation chain by forming stable phenoxyl radicals.[7]

We have no experimental evidence to propose a clear-cut reaction pathway. However, on the basis of experimental findings such as the reactivity order of tertiary C–H > secondary C–H ≫ primary C–H, as well as the ionic nature of the reaction, we propose the following reaction pathway. The metal catalyst reacted with TBHP to give its higher valent oxometal species which has already been proposed in a similar alkane oxidation using ruthenium(II) in connection with the cytochrome P-450 type mechanism.[8] Then hydride abstraction from an alkane by this species and the oxygen transfer to the alkane occur simultaneously to give the corresponding alcohol which is further oxidised to the ketone.

Oxidation of cyclohexane 1 with other oxidising agents

When similar treatment of cyclohexane **1** with anhydrous TBHP–CH_2Cl_2[9] was carried out in the presence of Mn^{2+}–TSM, the product yields and turnover numbers were lower than those obtained in the oxidation with aqueous TBHP, probably because of a lower reaction temperature (Table 2, run 1). Here, the addition of water to the reaction system further decreased the product yield (Table 2, run 2). On the other hand, in the oxidation with anhydrous TBHP the addition of MS 4 Å increased the product yield (Table 2, run 3), showing that MS 4 Å itself has a catalytic effect promoting oxidation besides dehydration. Other oxidising agents such as H_2O_2, PhIO, *m*-chloroperbenzoic acid (*m*-CPBA) and potassium peroxymonosulfate (OXONE) were also examined for this reaction, but they were revealed to be ineffective and unsuitable for this reaction system because these oxidising agents decomposed rather than oxidised the alkanes.

Conclusions

Cyclohexane **1** was oxidised to cyclohexanone **2** and cyclohexanol **3** in the presence of M^{n+}–TSM (M^{n+} = Mn^{2+}, Cr^{3+}, Co^{2+} and Cu^{2+}) and MS 4 Å in 9.7–13.4% GLC yield with turnover numbers 154–205. Similarly, other alkanes **4**, **7**, **10**, **14**, **18** and **23** were oxidised mainly to the corresponding ketones in the presence of Mn^{2+}–TSM with a turnover number up to 435. The distribution of oxidation products from **10**, **14**, **18** and **23** indicated that the reactivity of the C–H bond of alkane was in the order of tertiary C–H > secondary C–H ≫ primary C–H. It was confirmed in the cyclohexane oxidation that Mn^{2+}–TSM was regenerated and reused. Compounds **1**, **4** and **10** were shape-selectively oxidised in the presence of Cr^{3+}–TSM.

Experimental

NMR spectra were recorded on a JEOL EX-400 (^{1}H NMR, 400 MHz; ^{13}C NMR, 100 MHz) instrument for solutions in $CDCl_3$ with Me_4Si as an internal standard. Coupling constants, *J*, are given in Hz. Mass spectra were measured on a Shimadzu QP-5000S mass spectrometer equipped with a Shimadzu GC-17 gas–liquid chromatograph (30 m × 0.254 mm, 0.25 µm film thickness, J&W Scientific fused silica capillary column DB-1) with electron-impact method for ionisation (ionising voltage, 70 eV). GLC analyses were performed on a Shimadzu GC-14A instrument (25 m × 0.33 mm, 5.0 µm film thickness, Shimadzu fused silica capillary column HiCap CBP10-S25-050) with flame-ionisation detectors and helium as the carrier gas. GLC yields were determined using acetophenone, octan-2-yl acetate or cyclohexyl phenyl ketone as an internal standard. X-ray powder diffraction (XRD) data were obtained on a Shimadzu XD-D1 diffractometer using Cu-Kα radiation and an energy dispersive detector. X-ray fluorescence (XRF) analyses were carried out at the Environment Preservation Center of Kyoto University.

Commercially available organic compounds except for TBHP were purified by the known method before use.[10] Commercially available inorganic compounds were used without further purification except for MS 4 Å and $Fe(acac)_3$. Powdered MS 4 Å was heated by a burner for at least 3 h and then cooled in a desiccator.[10] $Fe(acac)_3$ was recrystallised from ethanol.[10] M^{n+}–TSM (M^{n+} = Mn^{2+}, Cr^{3+}, Co^{2+} and Cu^{2+})

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			113
2	**1**	Mn^{2+}-TSM	(0.060) 1st	0	8.6	1.1			31
3	**1**	Mn^{2+}-TSM	(0.059) 2nd[e]	0	5.4	1.0			20
4	**1**	Mn^{2+}-TSM	(0.051) 3rd[e]	0	6.1	1.7			27
5	**1**	Mn^{2+}-TSM	(0.012)	0.10	7.7	0.9			136
6	**1**	Mn^{2+}-TSM	(0.012)	0.50	8.5	0.8			148
7	**1**	Mn^{2+}-TSM	(0.012)	1.00	11.2	2.2			205
8	**1**	Mn^{2+}-mont	(0.012)	0	0.3	0.5			9
9	**1**	Mn^{2+}-mont	(0.012)	1.00	7.9	1.1			141
10	**1**	—		0	0.4	0.3			—
11	**1**	—		1.00	0.1	0.2			—
12	**1**	MnO_2	(0.012)	0	0.7	0.5			16
13	**1**	MnO_2	(0.012)	1.00	7.5	1.9			141
14	**1**	Na^{2+}-TSM	(0.230)	0	0.7	0.1			0
15	**1**	Na^{2+}-mont	(0.115)	0	0.1	0.1			0
16	**1**	Cr^{3+}-TSM	(0.012)	1.00	10.2	0			170
17	**1**	Co^{2+}-TSM	(0.012)	1.00	8.9	0.8			155
18	**1**	Cu^{2+}-TSM	(0.012)	1.00	8.8	0.9			154
					5	**6**			
19	**4**	Mn^{2+}-TSM	(0.012)	1.00	21.2	3.7			384
20	**4**	Mn^{2+}-mont	(0.012)	1.00	17.5	3.0			317
21	**4**	—		1.00	1.2	0.9			—
22	**4**	MnO_2	(0.012)	1.00	5.6	1.9			109
23	**4**	Cr^{3+}-TSM	(0.012)	1.00	35.8	1.3			608
					8	**9**			
24	**7**	Mn^{2+}-TSM	(0.012)	1.00	17.8	4.6			335
25	**7**	Mn^{2+}-mont	(0.012)	1.00	17.9	4.9			339
26	**7**	—		1.00	1.7	0.6			—
27	**7**	MnO_2	(0.012)	1.00	15.1	6.2			303
					11	**12**	**13**		
28	**10**	Mn^{2+}-TSM	(0.012)	1.00	26.1	12.7	0.7		435
29	**10**	Mn^{2+}-mont	(0.012)	1.00	27.6	7.7	0.3		361
30	**10**	—		1.00	1.3	0.5	< 0.1		—
31	**10**	MnO_2	(0.012)	1.00	8.7	2.5	0.2		116
32	**10**	Cr^{3+}-TSM	(0.012)	1.00	1.9	1.3	< 0.1		38
33	**10**	Co^{2+}-TSM	(0.012)	1.00	18.1	5.1	0.4		239
34	**10**	Cu^{2+}-TSM	(0.012)	1.00	17.7	4.3	0.3		222
					15	**16**	**17**		
35	**14**	Mn^{2+}-TSM	(0.012)	1.00	2.9	2.0	1.9		57
36	**14**	Mn^{2+}-mont	(0.012)	1.00	3.2	2.1	2.0		61
37	**14**	—		1.00	1.5	1.0	1.0		—
38	**14**	MnO_2	(0.012)	1.00	4.1	2.7	2.6		78
39	**14**	Cr^{3+}-TSM	(0.012)	1.00	2.9	2.3	2.2		62
					19	**20**	**21**	**22**	
40[f]	**18**	Mn^{2+}-TSM	(0.060)	5.00	5.3	0.8	2.7	1.3	84
					24	**25**	**26**	**27**	
41[f]	**23**	Mn^{2+}-TSM	(0.060)	5.00	3.7	1.6	0.5	0.2	86

[a] Reaction conditions: alkane (10.0 mmol), 70% aqueous TBHP (45.0 mmol), catalyst, MS 4 Å (1.00 g), benzene (4.0 cm^3) at 60 °C for 48 h. [b] Of cations. [c] Based on alkane. [d] Based on the amount of cations (see Experimental section). [e] The catalyst was washed with acetone and dried before use. [f] Five times scale.

was prepared by treatment of Na$^+$–TSM (commercial white powder or 10% aqueous gel: Topy) with $Mn(NO_3)_2{\cdot}6H_2O$, $Cr(NO_3)_3{\cdot}9H_2O$, $Co(NO_3)_2{\cdot}6H_2O$ and $Cu(NO_3)_2{\cdot}3H_2O$, respectively, in aqueous acetone as described elsewhere.[3a,5,11] The colour of Mn^{2+}–, Cr^{3+}–, Co^{2+}– and Cu^{2+}–TSM was pale yellow–brown or beige, pale blue, beige and pale blue, respectively. M^{n+}–mont (M^{n+} = Mn^{2+}, Fe^{3+}, Al^{3+} and Ce^{3+}) was prepared by the previously reported method from Na$^+$–mont (Kunipia G: commercial white powder: Kunimine) and metal nitrate in aqueous acetone.[3a,3b,5] The absence of the cation in the last aqueous washing in the catalyst preparation was confirmed by quantitative or qualitative analysis of respective ions.[12] The basal spacings (d_{001}) of Mn^{2+}–TSM, Cr^{3+}–TSM, Co^{2+}–TSM, Cu^{2+}–TSM, Na$^+$–TSM, Mn^{2+}–mont and Na$^+$–mont were estimated to be 14.3, 14.0, 14.4, 14.1, 9.6, 14.9 and 9.6 Å, respectively, by a sharp peak obtained on XRD analysis, showing clearly that the catalysts have an interlayer structure. The amount of cations of Mn^{2+}–TSM, Cr^{3+}–TSM, Co^{2+}–TSM, Cu^{2+}–TSM and Mn^{2+}–mont were estimated by XRF analysis of a solution of the catalyst in 47% aqueous HF to be 0.115, 0.392, 0.300, 0.301 and 0.300 mmol g^{-1}, respectively. Commercially available montmorillonite K10 (light grey powder: Aldrich), *i.e.* H$^+$–mont, was used without further activation. Anhydrous TBHP–CH_2Cl_2 was prepared and titrated by the reported method.[9] All the products except for 2,5-dimethylhexan-3-one **26** are commercially available. Compound **26** was prepared by pyridinium chlorochromate (PCC) oxidation[13] of 2,5-dimethylhexan-3-ol **27** and determined by ^1H NMR, ^{13}C NMR and MS:[14] a colourless oil; δ_H(400 MHz, $CDCl_3$) 0.91 (6 H, d, *J* 6.8), 1.08 (6 H, d, *J* 6.8),

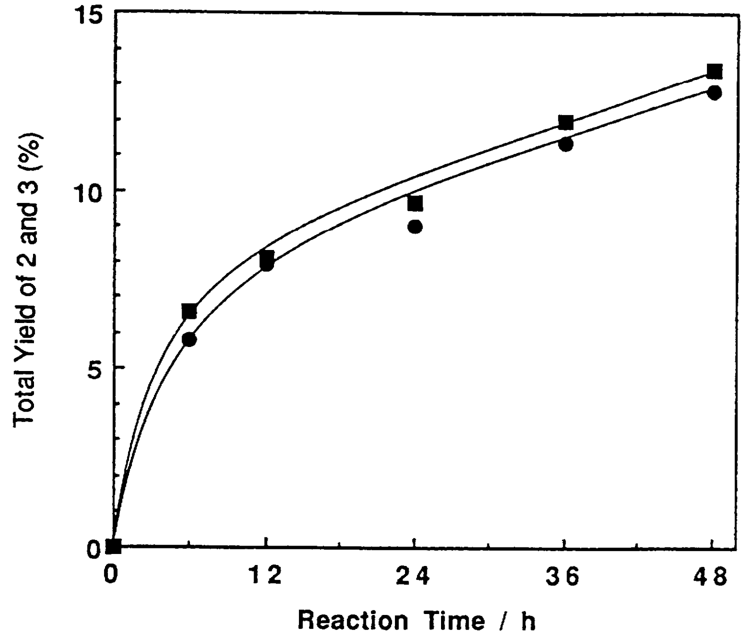


Fig. 1 Time course of oxidation of cyclohexane **1** (10.0 mmol) with 70% aqueous TBHP (45.0 mmol) in benzene (4.0 cm^3) in the presence of Mn^{2+}–TSM (0.012 mmol) and MS 4 Å (1.00 g) at 60 °C (■) and in the presence of Mn^{2+}–TSM (0.012 mmol), MS 4 Å (1.00 g) and 2-*tert*-butyl-6-methylphenol (0.2 mmol) at 60 °C (●)

Table 2 Catalytic oxidation of cyclohexane **1** with anhydrous TBHP[a]

Run	Catalyst	(mmol)[b]	MS 4 Å/g	Products GLC yield (%)[c] 2	3	Turnover number[d]
1	Mn^{2+}–TSM	(0.012)	0	0.2	0.8	10
2[e]	Mn^{2+}–TSM	(0.012)	0	0.3	0.1	6
3	Mn^{2+}–TSM	(0.012)	1.00	4.2	1.0	78
4	—	—	0	< 0.1	< 0.1	—
5	—	—	1.00	< 0.1	< 0.1	—

[a] Reaction conditions: cyclohexane **1** (10.0 mmol), anhydrous TBHP–CH_2Cl_2 (45.0 mmol), catalyst, MS 4 Å, benzene (4.0 cm^3) at 40 °C for 48 h. [b] Of cations. [c] Based on **1**. [d] Based on the amount of cations (see Experimental section). [e] Water (1.0 cm^3) was added.

2.16 (1 H, m), 2.33 (2 H, d, *J* 6.8) and 2.57 (1 H, septet, *J* 6.8); δ_C(100 MHz, $CDCl_3$) 18.1 (q), 22.6 (q), 24.4 (d), 41.1 (d), 49.5 (t) and 214.6 (s); *m*/*z* 128 (M^+, 5%), 85 (28) and 57 (100).

General procedure for oxidation of alkanes with 70% aqueous TBHP in the presence of M^{n+}–TSM

A typical procedure using Mn^{2+}–TSM is described below (Table 1, run 28). To a mixture of adamantane **10** (1.36 g, 10.0 mmol), benzene (4.0 cm^3) and commercially available 70% aqueous TBHP (5.79 g, 45.0 mmol) were added powdered MS 4 Å (1.00 g) and Mn^{2+}–TSM (100 mg, 0.012 mmol as Mn^{2+}) in 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 **11** (397.7 mg, 2.61 mmol, 26.1%), adamantan-2-one **12** (191.1 mg, 1.27 mmol, 12.7%) and adamantan-2-ol **13** (10.9 mg, 0.07 mmol, 0.7%): total yield 39.5%, turnover number 435.

Mn^{2+}–TSM was regenerated by washing with acetone (10 cm^3) at room temperature for 24 h with magnetic stirring, followed by its filtration and by drying at 120 °C in an electric oven for 24 h.

Oxidation of octane 14 with 70% aqueous TBHP in the presence of Mn^{2+}–TSM followed by reduction with LAH

The reaction was similarly carried out using octane **14** in place of adamantane **10** (Table 1, run 35), and the combined filtrate and washings were poured slowly into saturated aqueous Na_2SO_3 (200 cm^3) and extracted with diethyl ether (3 x 50 cm^3). The extract was washed with brine and dried ($MgSO_4$). After removal of the solvent, the resulting colourless oil was dissolved in diethyl ether (20 cm^3), added portionwise with LAH (380 mg, 10.0 mmol) with cooling in an ice bath and stirred at room temperature for 24 h. The mixture was added with 10% aqueous HCl (200 cm^3) to remove excess LAH and extracted with diethyl ether (3 x 50 cm^3). The extract was neutralised with aqueous $NaHCO_3$, washed with brine and dried ($MgSO_4$). The products in the solution were determined by GLC analysis with 1-methylheptyl acetate as an internal standard. Methylcyclohexane **18** was similarly treated and a mixture of **19**, 2-methylcyclohexan-1-ol **20**, 3-methylcyclohexan-1-ol **21** and 4-methylcyclohexan-1-ol **22** was isolated. The distribution of **19**–**22** was estimated by comparison of the signal intensity of the carbon attached to the hydroxy group (each signal was assigned by comparison with that of the authentic commercial **19**–**22**), measured by the gated decoupling method with $Fe(acac)_3$ as a relaxation reagent in a quantitative ^{13}C NMR analysis.[15]

Oxidation of cyclohexanol 3 with 70% aqueous TBHP in the presence of Mn^{2+}–TSM

Cyclohexanol **3** was treated according to the general oxidation procedure of adamantane **10**; cyclohexanone **2** (669.0 mg, 6.82 mmol, 68.2%), conversion 85.1%, turnover number 568. A similar treatment without the addition of Mn^{2+}–TSM afforded 196.4 mg (2.00 mmol, 20.0%) of **2** with 34.5% conversion of **3**.

Determination of turnover number

We defined a turnover number as follows: (turnover number) = {2 × [the amount of ketone (mmol)] + [the amount of alcohol (mmol)]}/[the amount of cations (mmol)]. In the cases of octane **14** and methylcyclohexane **18**, the real turnover numbers must be higher than those calculated here, because the main products from **14** and **18** were ketones which were reduced to alcohols for convenience of GLC determination.

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