Preparation and catalysis of DMY and MCM-41 encapsulated cationic Mn(III)–porphyrin complex

Zhen Li, Chun-Gu Xia[*], Xiao-Ming Zhang

*State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics,
Chinese Academy of Sciences, Lanzhuo 730000, China*

Abstract

The synthesis and characterization of the cationic manganese–porphyrin [*meso*-tetrakis(1-methyl-4-pyridinio)porphyrinato] manganese(III) penta-acetate complexes encapsulated in zeolite and mesoporous molecular sieve has been accomplished, and their catalytic activity was tested in the epoxidation of styrene and cyclohexene by iodosylbenzene. With mesoporous molecular sieve (MCM-41) and the new NaY zeolite (DMY) as supports, the encapsulated manganese–porphyrin systems show high activity and selectivity for the epoxidation. The effects of solvent and reaction time and the performance of the recovered catalysts have been studied. The mechanism of olefin oxidation has also been discussed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Zeolite; Molecular sieve; Manganese–porphyrin; Iodosylbenzene; Epoxidation

1. Introduction

The development of efficient oxidation catalysts which mimic the mono-oxygenase cytochrome P-450 has received a lot of attention in recent years [1–4]. As biomimetic catalysts in the oxygenation of hydrocarbons, metalloporphyrin complexes have been largely employed during the past two decades. The high efficiency of some of these catalysts makes them potentially useful for large-scale oxidations.

Immobilization of expensive metalloporphyrin catalysts on insoluble organic and inorganic supports appears to be a good way to render them practicable and improve their stability, selectivity because of the support environment and other advantages with respect to recovery and reuse. Supporting metallo-

porphyrins also provides a physical separation of active sites, thus minimizing catalyst self-destruction and dimerization of unhindered metalloporphyrins. Furthermore, in the era of "environmental amity chemistry", heterogeneous catalytic oxidations have become an important target since their process are used in industry, helping to minimize the problems of industrial waste treatment and disposal [5–9].

Mineral supports were selected because of their inertness in strongly oxidizing media. However, in the natural faujasite and synthetic zeolites X and Y, the inner diameter and channel diameter are in the range 0.7–1.3 nm. They are not available for big complexes because the limited pore size of these zeolites make it difficult for big complexes, substrates and products to diffuse into or out of the narrow channel of the microporous inorganic solid [10]. Up to now, a variety of mesoporous solids have been produced and are characterized by pore diameters that could be adjusted to between 1.8 and 20.0 nm [11]. In

* Corresponding author. Tel.: +86-931-827-6531;
fax: +86-931-827-7088.
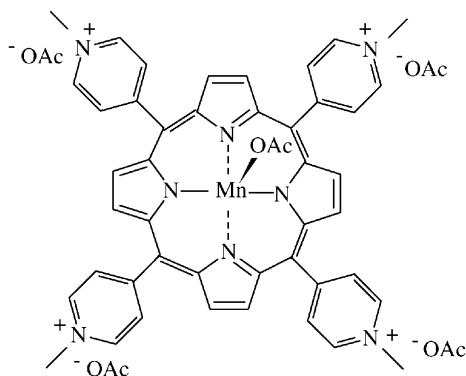*E-mail address:* cgxia@ns.lzb.ac.cn (C.-G. Xia).

Fig. 1. [*meso*-Tetrakis(1-methyl-4-pyridinio)porphyrinato]manganese(III)penta-acetate, MnTMPyP.

this work, we prepared two heterogeneous oxidation catalysts by anchoring a cationic manganese–porphyrin [*meso*-tetrakis(1-methyl-4-pyridinio)porphyrinato] manganese(III) penta-acetate complex (Fig. 1) into mesoporous molecular sieve (MCM-41) and new NaY zeolite (DMY). The encapsulated Mn–porphyrin catalysts exhibits enhanced stability, as well as good catalytic activity and selectivity in the epoxidation of styrene and cyclohexene by iodosylbenzene (PhIO) in organic media.

2. Experimental

2.1. Materials and equipment

5,10,15,20-Tetrakis(1-methyl-4-pyridinio)porphyrin (TMPyPH$_2$), iodosylbenzenediacetate were purchased from Fluka. Styrene and cyclohexene were first washed with 10% sodium hydroxide and then distilled over calcium hydride. The zeolite-Y of expanded cage (DMY) was obtained from Lanzhou Lianyou General Factory: surface area 864 m^2/g, SiO$_2$/Al$_2$O$_3$ = 83/13 (g/g), pore diameter distribution 1–3 nm. Mesoporous molecular sieve (MCM-41), which was prepared according to the literature [12], was dried by heated at 450 °C for 6 h, surface area 719 m^2/g, average pore diameter 21.8 Å and Si/Al atomic ratio 35. All other reagents used were of AR grades of purity.

FT-IR spectra (KBr disks) were measured on a Bruker IFS 120HR FT-IR spectrophotometer. X-ray powder diffraction patterns were obtained on a

D/Max-RB X-ray diffractometer. XPS measurements were performed with a VG Scientific ESCALAB 210 instrument with Mg Kα radiation (1253.6 eV). UV–Vis spectra were obtained with a Hewlett-Packard 8453 spectrophotometer. Solid diffuse-reflectance UV/Vis spectra were measured by Shimadzu UV-240. The reaction products of oxidation were determined and analyzed by HP 5890 II gas chromatograph and HP 6890/5973 GC/MS.

2.1.1. Preparation of [Mn^{III}(TMPyP)](OAc)$_5$

100 mg (73.33 μmol) of TMPyPH$_2$ and 10 equivalent of Mn(OAc)$_2$·4H$_2$O were dissolved in 30 ml of glacial acetic acid and heated to 80 °C for 6 h. After cooling, the solvent was removed under reduced pressure and the dark solid was precipitated by addition of a mixture MeOH/Et$_2$O (1/4) giving 170 mg of MnTMPyP. (The UV–Vis spectrum of MnTMPyP is similar to that described by Harriman and Porter [13].)

2.1.2. Preparation of encapsulated metalloporphyrin

A suspension of DMY (250 mg) in MeOH (10 ml), containing Mn^{III}(TMPyP) (0.24 mmol), was stirred for 24 h at 20 °C. The resulting materials was filtered and washed with CH$_2$Cl$_2$ and MeCN until the filtrate become colorless. The solid obtained was dried at 100 °C for 4 h which afforded MnTMPyP/DMY. The methods of preparation of MnTMPyP/MCM-41 was similar to that reported above. The encapsulated manganese–porphyrin was characterized by FT-IR, XPS, DR-UV/Vis and X-ray diffraction spectra (XRD).

To calculate the amount of loaded MnTMPyP, a known amount of MnTMPyP/DMY or MnTMPyP/ MCM-41 was decomposed with concentrated and heated HCl in order to remove the MnTMPyP from the zeolite. UV–Vis spectra of the removed MnTMPyP were recorded in aqueous solutions (pH ∼ 2) and the absorbance of the Soret band was used to evaluate the loading of MnTMPyP per gram of MnTMPyP/DMY and MnTMPyP/MCM-41, which proved to be 6.66 × 10^{-5} and 6.33 × 10^{-5} mol g^{-1}.

2.2. Oxidation reactions

Typically, the reactions were initiated by adding, under magnetic stirring, the solids iodosylbenzene (0.1 mmol) in a (3:1) dichloromethane–acetonitrile

mixture (2 ml) containing substrates (0.2 mmol), and catalyst (0.005 mmol), in a 25 ml glass flask. In the oxidation of styrene temperature was 0 °C. In the oxidation of cyclohexene temperature was 25 °C. After 8 h, the reaction products were analyzed by HP 5890 II GC with a 25 m × 0.32 mm SE54 column using decane as the internal standard. The yields were based on iodobenzene formed. Nitrogen was used as the carrier gas with an FID detector. The products were determined by GC/MS system.

For the recycling experiments, the catalyst was washed five times with 2 ml of methanol. This catalyst was then dried for 3 h at 30 °C, before the next recycling.

3. Results and discussion

3.1. Characterization of the supported metalloporphyrin

The catalysts obtained were characterized by various techniques such as FT-IR, XPS, DR-UV/Vis and XRD.

Fig. 2 shows the IR spectra for the free MnTMPyP complex and for encapsulated MnTMPyP. The zeolite/molecular sieve band dominates this region of the spectrum; however, the presence of MnTMPyP is obvious, because there is no band observed in the region 1600–1200 cm^{-1} in the spectra of supports. MnTMPyP/DMY and MnTMPyP/MCM-41 show bands at 1447, 1427 and 1577 cm^{-1}. These bands are due to the stretching vibrations of the C=N and C=C bonds.

X-ray powder diffraction (XRD) patterns of the encapsulated MnTMPyP are given in Fig. 3, which are in excellent agreement with the XRD pattern for unloaded zeolite/molecular sieve without any peaks arisen from MnTMPyP. This suggests that the solid support is structurally unchanged and the manganese–porphyrin should be dispersed molecularly within the channels.

The XPS spectra also provide information on encapsulation (Fig. 4). From the data of XPS (Table 1), it can be seen that Mn_{2p} and pyrrole N_{1s} binding energies in encapsulated MnTMPyP are lower than those in free MnTMPyP. The O_{1s} binding energies in encapsulated MnTMPyP are 532.28 and 532.94 eV, respectively,

3750 3500 3250 3000 2750 2500 2250 2000 1750 1500 1250 1000 750
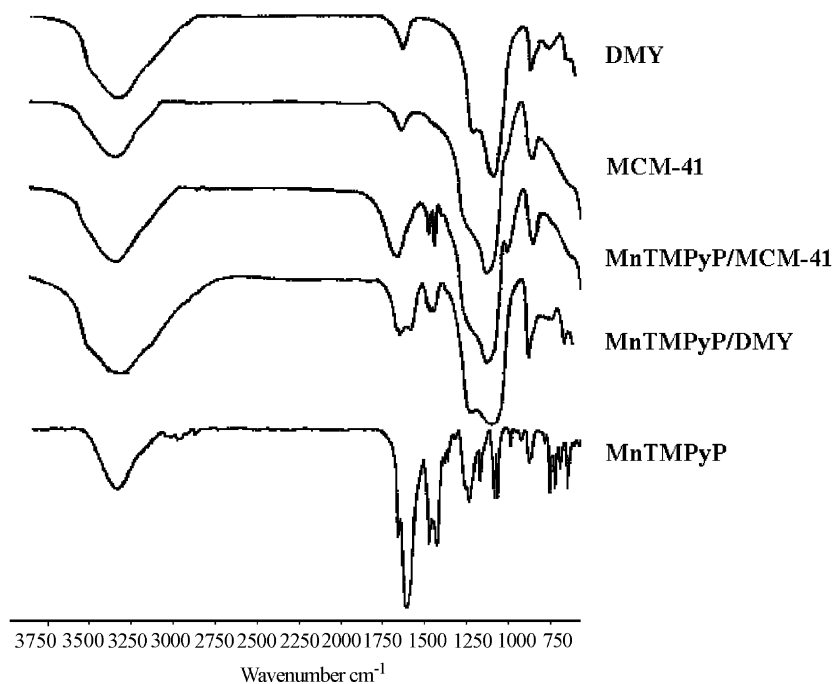
Wavenumber cm^{-1}

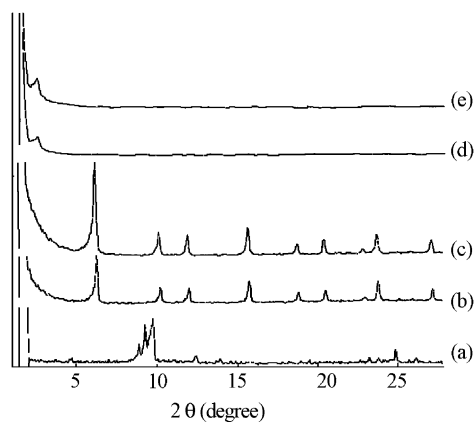Fig. 2. FT-IR spectra of free MnTMPyP and encapsulated MnTMPyP.

Fig. 3. XRD patterns of: (a) MnTMPyP, (b) MnTMPyP/DMY, (c) DMY, (d) MnTMPyP/MCM-41, (e) MCM-41.

which are lower than those of supports. The difference in pyridine N_{1s} binding energies between encapsulated MnTMPyP and free MnTMPyP is larger than 0.5 eV. These changes in binding energy can be attributed to charge transfer between O_{1s}, Mn_{2p} and pyrrole N_{1s}. It is considered that MnTMPyP is anchored to the support through Mn–O ligation and electrostatic interaction between the MnTMPyP 4-N-methyl-pyridyl groups and the support anionic species.

The MnTMPyP encapsulated in zeolite and molecular sieve have been characterized by diffuse reflectance UV spectroscopy and the typical UV–Vis spectra are given in Fig. 5. The encapsulated MnTMPyP showed the Soret band at 465 nm which was the same as that in the spectra of the free MnTMPyP. This result indicates that the successful anchoring of MnTMPyP into the supports was achieved. Concerning the increase in the Q band for the encapsulated MnTMPyP, it is probably associated with the axial coordination of the

MnTMPyP to OH-containing ligands present in the zeolite.

3.2. Epoxidation of styrene and cyclohexene

3.2.1. The effect of different catalysts

The efficiencies of the manganese–porphyrins as catalysts for olefins epoxidation in solution and encapsulated in zeolite/molecular sieve were examined using styrene and cyclohexene as the substrates. The data are shown in Table 2.

Encapsulated catalysts MnTMPyP/DMY and MnTMPyP/MCM-41 give rise to higher activity and selectivity than the homogenous counterparts. This efficiency possibly arises from MnTMPyP coordination to zeolites, which renders them more resistant to oxidative self-destruction. From the results, it is evident that the catalyst MnTMPyP/DMY leads to styrene oxide yield similar to the catalyst MnTMPyP/MCM-41. However, for cyclohexene, MnTMPyP/MCM-41 gives higher epoxide yield than MnTMPyP/DMY. Maybe the structural difference between DMY and MCM-41 induced this result. After using MnTMPyP/DMY and MnTMPyP/MCM-41 as catalysts, the resultant solution was measured by UV–Vis spectra. It is shown that a small quantity of MnTMPyP was leached from the support.

3.2.2. The effect of solvent

Fig. 6 shows the effect of different solvents on the oxidation of styrene and cyclohexene with PhIO in the presence of catalysts. Evidently, the dichloromethane–acetomitrile mixture (3:1) is a good solvent system for epoxidation of styrene, since the yield and selectivity of epoxide are high. In contrast, in the oxidation of cyclohexene the yield of epoxide increases with increasing polarity of the

Table 1
The data of X-ray photoelectron spectroscopy of DMY, MCM-41, MnTMPyP and encapsulated MnTMPyP

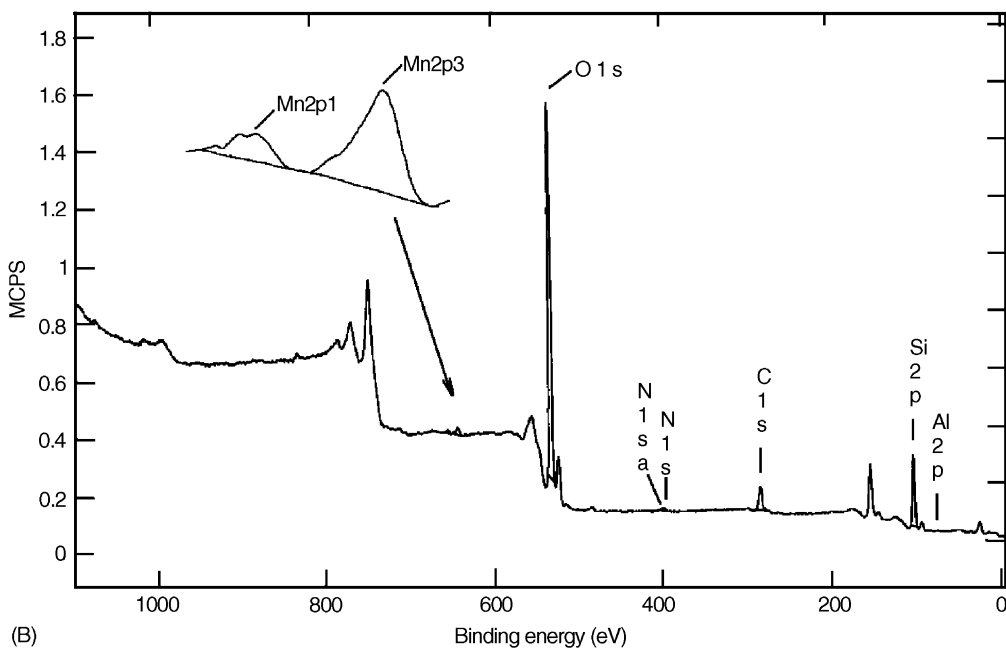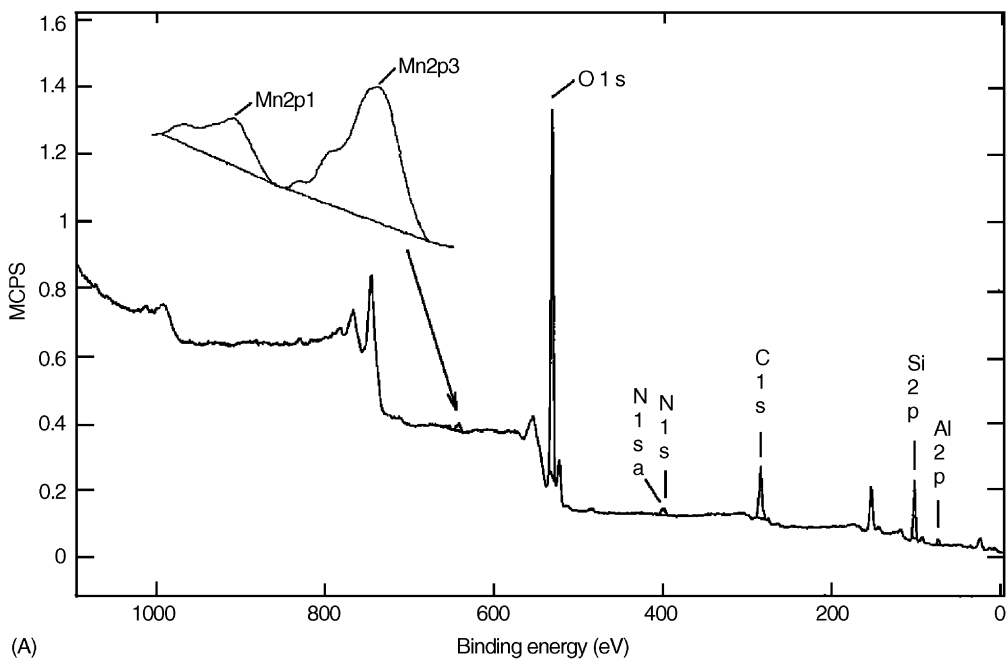| XPS peak	Binding energy (eV)				
	DMY	MCM-41	MnTMPyP	MnTMPyP/DMY	MnTMPyP/MCM-41
Pyridine N_{1s}	–	–	398.44	399.93	399.81
Pyrrole N_{1s}	–	–	401.92	400.18	401.14
$Mn_{2p1/2}$	–	–	653.83	653.38	653.20
$Mn_{2p3/2}$	–	–	641.96	641.93	641.56
O_{1s}	533.06	533.42	–	532.28	532.94

Fig. 4. XPS spectra of (A) MnTMPyP/DMY and (B) MnTMPyP/MCM-41.
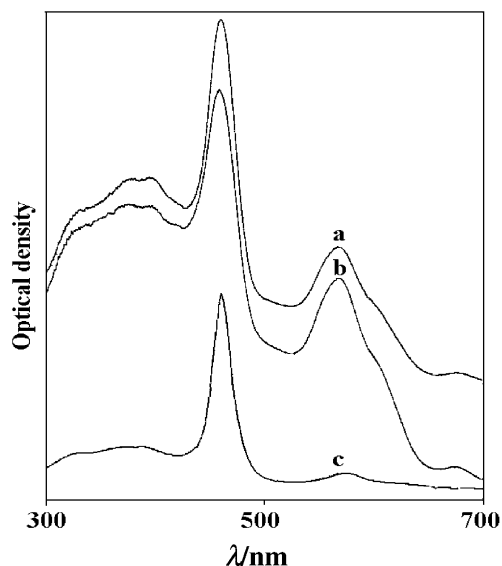
Fig. 5. Diffuse reflectance spectra of MnTMPyP/DMY (a), MnTMPyP/MCM-41 (b) and UV/Vis spectra of MnTMPyP in CH$_2$Cl$_2$/CH$_3$CN (v/v = 3/1) solution (c).

solvent, which has little effect on the selectivity of epoxide.

3.2.3. The effect of time

The effect of time on styrene and cyclohexene oxidation with PhIO in the presence of catalysts is shown in Fig. 7. It is clear that cyclohexene is easier to be

oxidized than styrene. We can observe an increase in epoxide yield with time for the two substrates. The major product after 8 h of reaction is always the epoxide (selectivity between 87 and 100%).

3.2.4. Reuse of the catalysts

The selectivity of encapsulated MnTMPyP has not changed after five times of reusing, but the catalytic activity drops. The result is given in Table 3. An increase in the yield between the reaction with the first and the second recycling is observed for styrene epoxidation catalyzed by MnTMPyP/DMY, giving an indication that the extraction procedure affects the catalyst, activating it. This was not observed for MnTMPyP/MCM-41, which presented a decrease in its activity from the first to the fifth recycling. The decrease in the activity could be attributed to the leaching or decomposition of MnTMPyP complex under reaction conditions.

3.2.5. Mechanism of olefin epoxidation

It is generally proposed in the literature that low levels of allylic oxidation and high levels of epoxidation indicate an active intermediate containing two oxidizing equivalents localized in the vicinity of the center of the catalyst (Type-1 intermediate) [14]. For manganese–porphyrin it is an oxomanganese(V)–porphyrin (OMn^{V}P) [15–17]. Further reactions of this species involve alkene oxidation, together with catalyst destruction and the oxidation

Table 2

Epoxidation of styrene and cyclohexene with PhIO by encapsulated MnTMPyP and free MnTMPyP[a]

Substrate	Catalyst	Epoxide yield (%)[b]	Selectivity (%)[c]		
			Epoxide	PhCHO	PhCOCH$_3$
Styrene[d]	MnTMPyP	43.9	86.5	2.17	11.3
	MnTMPyP/DMY	51.6	86.5	2.82	10.6
	MnTMPyP/MCM-41	51.0	100	–	–
			Epoxide	Cyclohex-2-en-1-one	Cyclohex-2-en-1-ol
Cyclohexene[e]	MnTMPyP	45.6	95.6	4.37	–
	MnTMPyP/DMY	65.4	100	–	–
	MnTMPyP/MCM-41	90.8	97.8	–	2.2

[a] Substrate/PhIO/MnTMPyP molar ratio = 40:20:1; solvent: 2 ml (CH$_2$Cl$_2$/CH$_3$CN = 3/1, v/v); time: 8 h.

[b] Based on iodobenzene formed using GC.

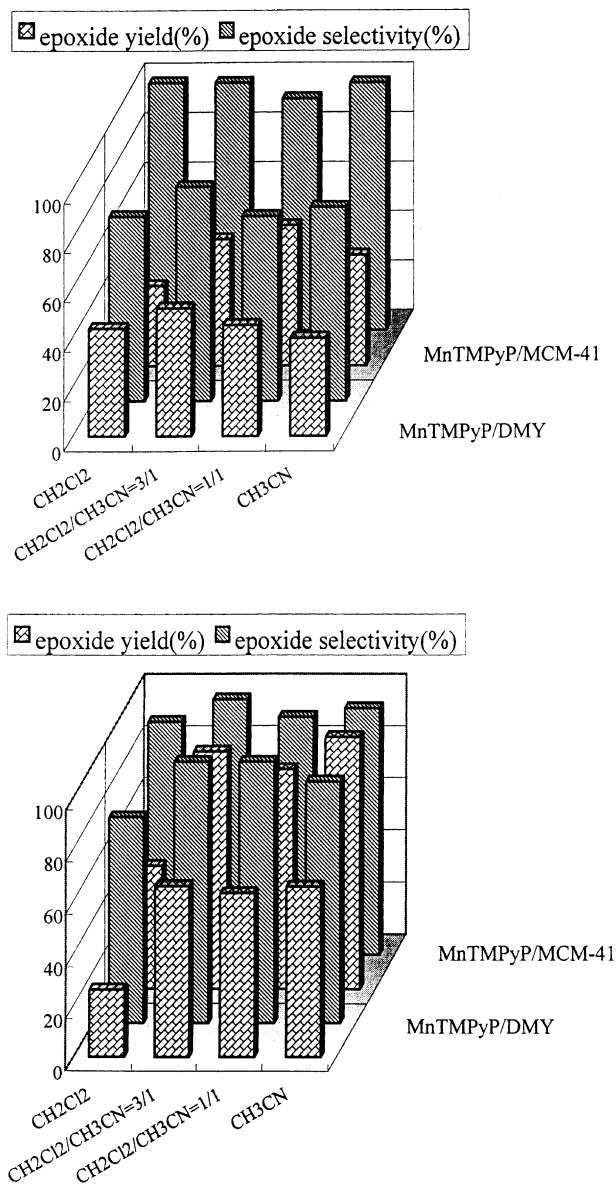[c] Selectivity determined by GC.

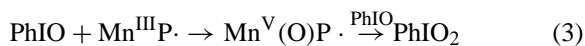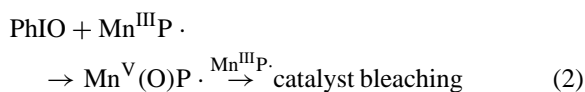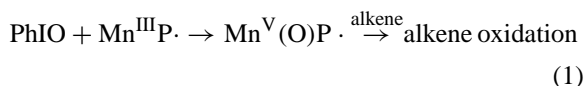[d] Temperature: 0 °C.

[e] Temperature: 20 °C.

Fig. 6. Effects of solvent on the epoxide yield and selectivity of styrene (upper) and cyclohexene (bottom).

of PhIO to $PhIO_2$ (reactions 1–3) [18,19].

$$PhIO + Mn^{III}P\cdot \rightarrow Mn^V(O)P\cdot \xrightarrow{alkene} alkene\ oxidation \tag{1}$$

$$PhIO + Mn^{III}P\cdot$$
$$\rightarrow Mn^V(O)P\cdot \xrightarrow{Mn^{III}P\cdot} catalyst\ bleaching \tag{2}$$

$$PhIO + Mn^{III}P\cdot \rightarrow Mn^V(O)P\cdot \xrightarrow{PhIO} PhIO_2 \tag{3}$$

For our encapsulated MnTMPyP-PhIO catalyst system, fairly good selectivities are obtained in the oxidation of styrene and cyclohexene. However, in all the reactions, PhIO was not totally consumed and the PhI yields were not 100%. This is due to a combination of
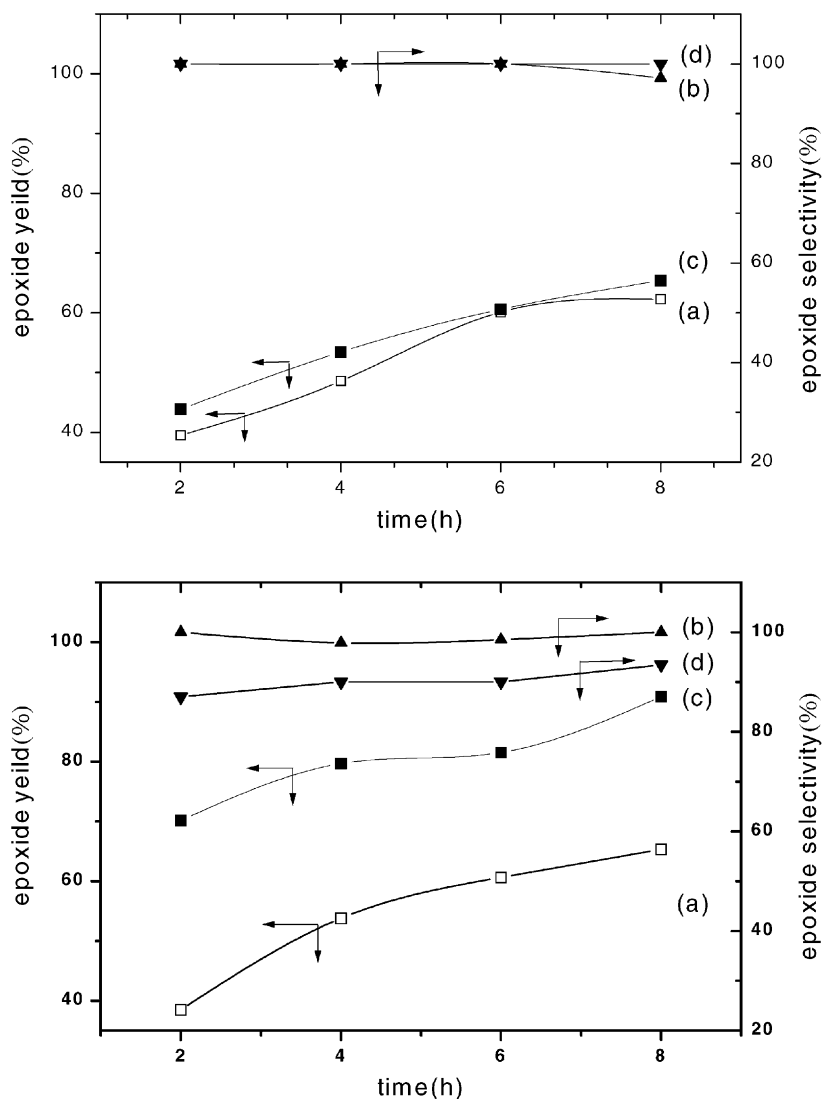
Fig. 7. Effect of time in the oxidation of styrene and cyclohexene with PhIO catalyzed by MnTMPyP/DMY (upper) and MnTMPyP/MCM-41 (bottom). (a) Epoxide yield of styrene; (b) epoxide selectivity of styrene; (c) epoxide yield of cyclohexene; (d) epoxide selectivity of cyclohexene.

factors, such as the low solubility of PhIO, or the slow diffusion of PhIO in zeolite/molecular sieve channels.

The first step in the reaction of the oxo-Mn(V) with alkenes has been postulated to be either direct attack to produce a radical (A), carbocation (B), or a metallacycle (C) or electron transfer to produce a caged pair (D) which collapses to one of these intermediates. Rearrangements which accompany epoxidation suggest an intermediate carbocation arising from caged pair collapse or metallacycle opening (Fig. 8) [20].

As observed for styrene and cyclohexene, the catalytic efficiency of the supported cationic manganese–porphyrin is increased by comparison with the homogeneous reaction. This is because anchoring the catalyst prevents MnTMPyP aggregation through π–π interaction, mitigating catalyst deactivation.

Table 3
The catalytic activity of MnTMPyP encapsulated in DMY and MCM-41 during the recycling in styrene and cyclohexene epoxidation[a]

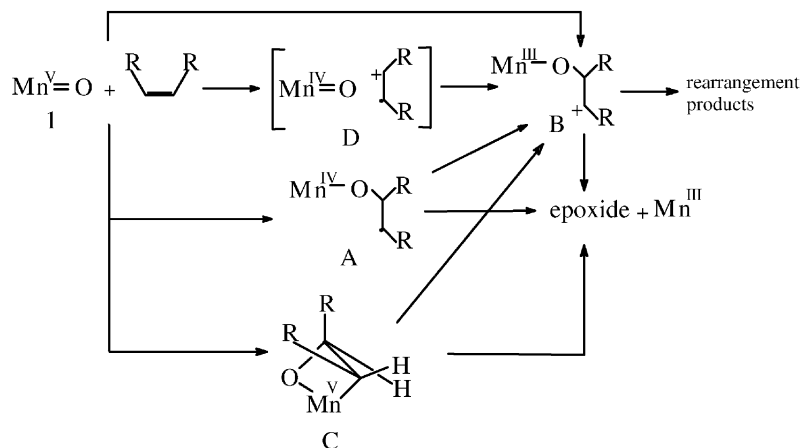| Recycling number	Catalyst	Styrene epoxide		Cyclohexene epoxide	
		Yield (%)	Selectivity (%)	Yield (%)	Selectivity (%)
1	MnTMPyP/DMY	51.6	86.5	65.4	100
2		75.7	89.4	45.4	100
3		60.8	85.9	56.5	100
4		61.5	86.1	56.0	100
5		61.5	86.7	56.7	100
1	MnTMPyP/MCM-41	51.0	100	90.8	97.8
2		45.7	100	82.2	86.1
3		48.4	97.7	71.6	87.8
4		44.6	95.9	64.9	91.9
5		44.5	100	77.0	94.1

[a] Conditions as in Table 2.

Fig. 8. Stepwise mechanisms for oxygen insertion into alkenes.

4. Conclusion

Binding cationic MnTMPyP to MCM-41 mesoporous molecular sieve and a new kind of Y-zeolite (DMY) leads to very efficient catalysts that can be easily recovered and re-used. The loss of activity after prolonged/repeated usage is attributed to catalyst leaching and/or decomposition of Mn–porphyrin complex, which demands further improvement. Irrespective of this, the supported MnTMPyP-PhIO system is highly active, also selective, simple, and safe to operate. We anticipate that the present heterogeneous catalytic system would be potentially applicable to practical organic synthesis.

Acknowledgements

References

[1] D. Mansuy, Coord. Chem. Rev. 125 (1993) 129.
[2] F. Montanari, L. Casella (Ed.), Metalloporphyrins Catalyzed Oxidations, Kluwer Academic Publishers, Dordrecht, 1994.
[3] R.A. Sheldon (Ed.), Metalloporphyrins in Catalytic Oxidations, Marcel Dekker, New York, 1994.
[4] B.A. Arndtsen, R.G. Bergman, T.A. Mobley, T.H. Peterson, Acc. Chem. Res. 28 (1995) 154.

[5] P. Battioni, J.P. Lallier, L. Barloy, D. Mansuy, J. Chem. Soc., Chem. Commun. (1989) 1149.

[6] E. Polo, R. Amadelli, V. Carassiti, A. Maldotti, Inorg. Chim. Acta 192 (1992) 1.

[7] P.E.F. Neys, A. Severeyns, I.F.J. Vankelecom, E. Ceulemans, W. Dehaen, P.A. Jacobs, J. Mol. Catal. A 144 (1999) 373.

[8] C.M.C.P. Manso, E.A. Vidoto, F.S. Vinhado, H.C. Sacco, K.J. Ciuffi, P.R. Martins, A.G. Ferreira, J.R. Lindsay, O.R. Nascimento, Y. Iamamoto, J. Mol. Catal. A 150 (1999) 251.

[9] I.L. Viana, C.M.C.P. Manso, O.A. Serra, Y. Iamamoto, J. Mol. Catal. A 160 (2000) 199.

[10] H. Norman, J. Coord. Chem. Soc. 19 (1988) 25.

[11] X.-M. Zhang, Z.-R. Zhang, J.-S. Suo, S.-B. Li, J. Mol. Catal. China 11 (3) (1997) 230.

[12] Z.-R. Zhang, J.-S. Suo, X.-M. Zhang, S.-B. Li, Acta Physico-Chimica Sinica 14 (1998) 243.

[13] A. Harriman, G. Porter, J.C.S. Faraday II 75 (1979) 1532.

[14] M.J. Gunter, P. Turner, J. Mol. Catal. 66 (1991) 121.

[15] B. Meunier, Chem. Rev. 92 (1992) 1411.

[16] T.G. Traylor, Pure Appl. Chem. 63 (1991) 265.

[17] M.J. Gunter, P. Turner, Coord. Chem. Rev. 108 (1991) 151.

[18] M.J. Nappa, C.A. Tolman, Inorg. Chem. 24 (1985) 4711.

[19] P. Inchley, J.R.L. Smith, New J. Chem. 13 (1989) 669.

[20] R.D. Arasasingham, G.-X. He, T.C. Bruice, J. Am. Chem. Soc. 115 (1993) 7985.