Enantioselective epoxidation of (*Z*)-stilbene using a chiral Mn(III)–salen complex: effect of immobilisation on MCM-41 on product selectivity

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Received (in Cambridge, UK) 17th July 2000, Accepted 10th August 2000
Published on the Web 18th September 2000

Manganese-exchanged Al-MCM-41 modified by the chiral salen ligand [(*R*,*R*)-(−)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)cyclohexane-1,2-diamine] has been investigated as a heterogeneous catalyst for the enantioselective epoxidation of (*Z*)-stilbene using iodosylbenzene as oxygen donor, with particular interest in the effect of reaction conditions on the *cis*:*trans* ratio of the epoxide product. Immobilisation of the chiral Mn–salen complex in Al-MCM-41 increases the *cis*:*trans* ratio of the epoxide product when compared to the non-immobilised complex under the same conditions. Increasing the level of Mn-exchange in the Al-MCM-41 increases the amount of *trans*-epoxide, whereas increasing the iodosylbenzene:substrate ratio increases the amount of *cis* product formed. Increasing the reaction temperature also increases the amount of *trans*-epoxide for the homogeneous Mn-complex under the same conditions. A series of experiments is described in which the external ion-exchange sites on Al-MCM-41 are preferentially silanised, which enables the *cis*/*trans* selectivity for external and internal sites to be determined. Mn–salen immobilised on the external surface of Al-MCM-41 gives the same *cis*:*trans* ratio as that observed with the non-immobilised Mn–salen complex in solution, whereas Mn–salen immobilised within the pores gives the *cis*-epoxide preferentially.

The enantioselection of the immobilised chiral Mn–salen complex is shown to decrease with reaction time at −10 °C, but the *cis*:*trans* epoxide ratio remains unchanged; whereas for the non-immobilised complex in solution the enantioselection is independent of reaction time. Iodobenzene, a decomposition product formed from iodosylbenzene, is found to act as a poison for the immobilised catalyst, leading to a slower reaction and lower enantioselection.

Introduction

In recent years, there has been considerable interest in the use of manganese–salen complexes for epoxidation of alkenes.[1–5] In particular, very high enantioselectivities are obtained for tri-substituted and (*Z*)-substituted alkenes using the Jacobsen and Katsuki type manganese(III)–salen complexes.[6–10] In view of the effectiveness of these homogeneous catalysts, there has been significant effort applied to the immobilisation of manganese(III)–salen complexes in order that they can be used as heterogeneous catalysts. A number of approaches have been attempted and the subject has recently been reviewed by Canali and Sherrington.[11] Considerable attention has been given to the support of these complexes on polymers.[12–14] Much less attention has been given to the use of inorganic supports such as zeolites and mesoporous MCM-41 materials.[15–19] Ogunwumi and Bein[17] showed that manganese(III)–salen complexes could be encapsulated in the pores of zeolite Y by appropriate synthetic methods. In addition, the ion-exchange of manganese(III) complexes into zeolite Y[18] or MCM-41[19] has been reported. Previously, we have shown[20,21] that ion-exchange of chiral manganese(III)–salen complexes onto Al-MCM-41 provides an effective heterogeneous enantioselective oxidation catalyst for (*Z*)-stilbene using iodosylbenzene as oxidant. In this paper, we extend this earlier study to investigate the effect of immobilisation of the chiral manganese(III)–salen complex on the *cis*:*trans* ratio of the epoxide product and the factors that affect the enantioselection of the oxidation process using immobilised complexes.

Results and discussion

Based on our previous studies using Cu-exchanged zeolite Y for the heterogeneous enantioselective aziridination of alkenes,[22,23] our initial studies for the immobilisation of Mn-complexes were based on the modification of Mn-exchanged zeolite Y with modifiers **1**–**4**, and the results are given in Table 1. In the absence of a modifier, Mn-exchanged zeolite Y was found to be inactive for the epoxidation of styrene and (*Z*)-stilbene using PhIO, $NaBO_3$, $LiClO_4$ and NaClO as oxidants in a range of solvents. Modifiers 2,2′-isopropylidenebis[(4*S*)-4-*tert*-butyl-2-oxazoline] **1**, and *trans*-1,2-diaminocyclohexane **2**, were also found to be inactive for the epoxidation of (*Z*)-stilbene using PhIO as oxygen donor. However, a very low activity was observed using 1,4,8,11-tetraazacyclotetradecane-5,7-dione, **3**, and 1,4,8,11-tetraazacyclotetradecane **4**, as modifiers. In view of the low yields of the epoxide obtained with these systems,

 DOI: 10.1039/b005752p

the investigation was redirected to the study of immobilised Mn(III)–salen complexes, which required the use of mesoporous MCM-41 in place of microporous zeolite supports.

The epoxidation of four alkenes was investigated using Mn-exchanged Al-MCM-41 modified with the chiral salen ligand [(*R*,*R*)-(−)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)cyclohexane-1,2-diamine] **5**, and the results are given in Table 2. The initial Mn exchange is carried out using Mn^{2+} with subsequent oxidation to Mn^{3+} on modification with the salen ligand. The best results were obtained with (*Z*)-stilbene although promising results were obtained with 1,2-dihydronaphthalene. In view of this, the subsequent studies were carried out using (*Z*)-stilbene as substrate, and representative results are shown in Table 3. As noted previously, immobilisation of Mn^{2+} within the mesopores of Al-MCM-41 leads to a significant enhancement in the activity for epoxidation, indicating a very strong interaction between the solvation sphere of the Mn^{2+} cation and the surface of Al-MCM-41. Interestingly, initially the *trans*-epoxide product is obtained with Mn-exchanged MCM-41 but, at longer reaction time, and hence higher conversion, the *cis* product dominates.[21] A similar activity and *cis*:*trans* ratio are observed when $Mn(OAc)_2$ is used as a homogeneous catalyst under identical conditions using CH_3CN as solvent; however, use of the chiral salen ligand either in the homogeneous or the heterogeneous system led to a marked enhancement in rate but with a significant difference in the *cis*:*trans* ratio of the epoxide product. In the homogeneous system, the *trans*-epoxide is the major product, whereas in the heterogeneous system it is the *cis* product that is preferred. Decreasing the initial ratio of (*Z*)-stilbene to oxidant leads to a decrease in reactivity for the heterogeneous system, together with a decrease in the total yield of the epoxide, an increase in the proportion of the *cis*-epoxide formed and a decrease in the ee for the *trans*-epoxide.

A series of experiments was conducted using Mn-exchanged Al-MCM-41 containing different concentrations of manganese. The results (Table 4) show that the enantioselection is not affected by the level of Mn exchange and the total yield is only marginally affected, with a slight decrease being observed at lower Mn concentrations. The *cis*:*trans* ratio of the epoxide

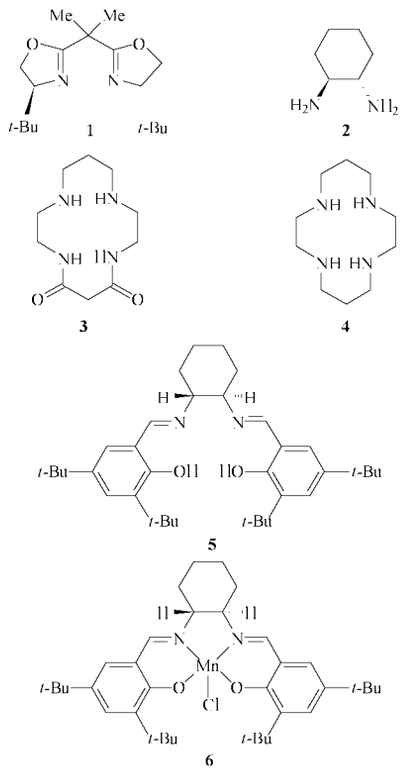


Table 1 Epoxidation of (*Z*)-stilbene at 25 °C using modified MnHY catalysts[a]

Modifier	Reaction time[b]/h	Epoxide yield (%)		
		Total	*cis*[c]	*trans*[c]
None	48	0	—	—
1	20	0	—	—
2	20	0	—	—
3	24	1	—	100
4	24	3	—	100

[a] (*Z*)-Stilbene–PhIO–catalyst = 7:1:0.13 in CH_2Cl_2. [b] Time taken for complete conversion of PhIO to PhI. [c] Normalised to 100% epoxide yield.

Table 2 Epoxidation of alkenes using Mn-Al-MCM-41–salen catalyst at 25 °C[a]

Alkene	Reaction time[b]/h	Epoxide yield (%)			Ee *trans* (%)
		Total	*cis*[c]	*trans*[c]	
(*Z*)-Stilbene	2	69	58	42	70
(*E*)-Stilbene	26	35	0	100	25
(*E*)-β-Methylstyrene	24	46.6	0	100	13
1,2-Dihydronaphthalene	4	67	100	0	54[d]

[a] Substrate–PhIO–catalyst = 7:1:0.13 in CH_2Cl_2 at 25 °C, catalyst Mn-exchanged Al-MCM-41 containing 2% Mn, refluxed with **5** for 24 h. [b] Time for complete conversion of PhIO to PhI. [c] Normalised to 100% epoxide. [d] Product has (1*R*,2*S*)-(+)-configuration.

Table 3 Epoxidation of (*Z*)-stilbene at 25 °C using Mn-Al-MCM-41–salen catalyst[a]

Catalyst	(*Z*)-Stilbene PhIO	Reaction time[b]/h	Epoxide yield (%)			Ee *trans* (%)
			Total	*cis*[c]	*trans*[c]	
None	7:1	25	0	—	—	—
Al-MCM-41	7:1	24	0	—	—	—
Mn-Al-MCM-41[d]	7:1	2[e]	3	—	100	—
		24	20	74	26	
Mn-Al-MCM-41 + salen[d,f]	7:1	2	69	58	42	70
	5:1	4	52.2	85	15	43
	3:1	4	46.8	83	17	45
	1:1	4	17.6	81	19	32
Mn-Al-MCM-41 + salen[f,g]	7:1	2	72	56	44	63
$Mn(OAc)_2$[h]	7:1	24	20.5	73	27	—
Mn–salen[i] complex	7:1	1	86	29	71	78

[a] PhIO–catalyst = 1:0.13 in CH_2Cl_2. [b] Time for complete conversion of PhIO to PhI, unless otherwise stated. [c] Normalised to 100% epoxide yield. [d] Mn-exchanged Al-MCM-41 containing 2% Mn. [e] 45% conversion of PhIO to PhI. [f] Mn-Al-MCM-41 refluxed with **5** for 24 h. [g] Reaction carried out under N_2. [h] Reaction carried out in CH_3CN, in CH_3OH or CH_2Cl_2, epoxide yield only 1.5%. [i] Homogeneous reaction of Mn complex, **6**.

Table 4 Effect of Mn concentration in Mn-Al-MCM-41 on the epoxidation of (*Z*)-stilbene[a]

Mn in Mn-Al-MCM-41[b] (%)	Epoxide yield (%)			Ee *trans* (%)
	Total	*cis*[c]	*trans*[c]	
2.6	72	56	44	70
2.0	69	58	42	70
1.6	64.6	75	25	70
1.2	62	84	16	70
0	0	—	—	—

[a] (*Z*)-Stilbene–PhIO–Mn = 7:1:0.13, the amount of catalyst added was adjusted to the required molar ratio, in CH_2Cl_2 at 25 °C for 24 h. [b] Determined by atomic absorption. [c] Normalised to 100% epoxide yield.

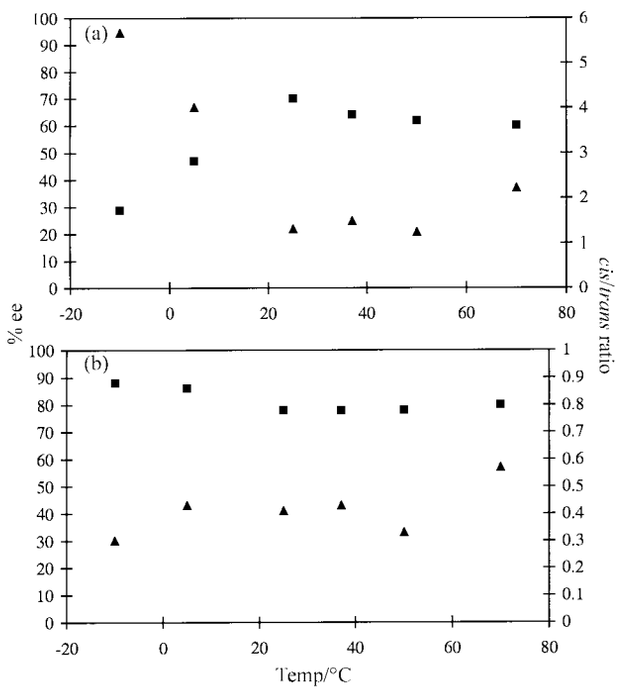


Fig. 1 Effect of temperature on epoxidation of (*Z*)-stilbene (a) heterogeneous catalyst Mn-Al-MCM-41 modified with (*R*,*R*)-(−)-ligand; (b) homogeneous catalyst Mn–salen complex **6**; reaction conditions: substrate–PhIO–catalyst, molar ratio = 7:1:0.13 in CH_2Cl_2; heterogeneous catalysts contain 0.1 mol ligand per mol Mn. Key: ▲ *cis*:*trans* ratio of epoxide; ■ ee of *trans*-epoxide (%).

product is significantly affected with the *cis*-epoxide becoming the major product at low Mn concentrations.

The effect of temperature on the *cis*:*trans*-epoxide product ratio and the ee of the *trans*-epoxide is shown in Fig. 1. For the homogeneously catalysed reaction using the chiral Mn–salen complex **6**, the *cis*:*trans* ratio and enantioselection are relatively insensitive to temperature, with a slight decrease in the yield and ee of the *trans*-epoxide being observed at higher temperatures. This is in marked contrast to the heterogeneous system (Fig. 1a) since, in this case, the formation of *trans*-epoxide increases at higher temperatures; however, the *cis*-epoxide is always the preferred product.

The co-ordination and reactivity of extraframework Mn^{2+} cations in aluminophosphate (AlPO) and silicon aluminophosphate (SAPO) materials have been widely investigated by EPR.[24–28] By comparison only a few studies have appeared on the EPR characterisation of Mn–salen complexes encapsulated in microporous materials.[29,30] In one such study, the disappearance of the Mn(II) ions from an initial MnY zeolite to the final Mn(III)–salenY sample was confirmed by EPR.[30] More recently, Bryliakov *et al.*[31] investigated the EPR spectra of a Mn(III)–salen complex in frozen solution, and reported a weak signal at

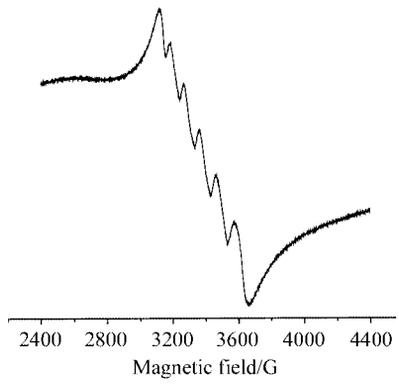
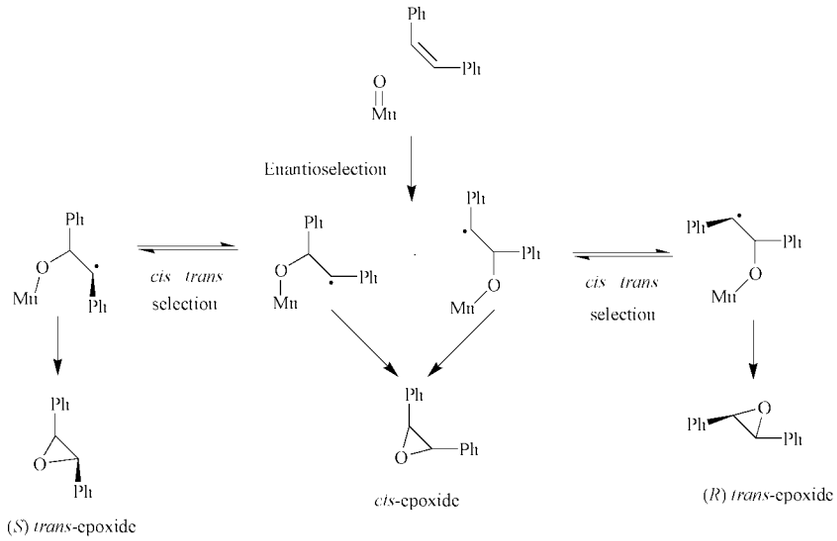


Fig. 2 X-Band EPR spectrum (10 K) of a Mn(II)-MCM-41 sample after refluxing for 2 days in the presence of the salen ligand.

$g = 8.0$ which they attributed to forbidden transitions within the $|\pm 2\rangle$ non-Kramers doublet of Mn^{III}. They also identified a resonance at $g = 5.7$ with a hyperfine splitting (hfs) of 73 G from the manganese nuclei of Mn^{IV} species, and observed changes to the shape of the Mn(III) EPR signal after addition of PhIO.[31] In the current study, a preliminary EPR analysis of the starting Mn(II)-MCM-41 sample was carried out after refluxing for 2 days in the presence of the salen ligand. A strong resonance at $g = 2.01$ with a hyperfine coupling of 91 G was observed (Fig. 2) which can be easily attributed to a distorted octahedral Mn^{II} species. The spin Hamiltonian parameters are also similar to those reported by Bryliakov *et al.*[31] for the homogeneous Mn(II)–salen complex, suggesting the formation of the Mn complex in the MCM-41 material. We are currently monitoring the redox changes to the complex during the reaction and plan to use ENDOR to explore the spatial orientation and interaction of the PhIO and stilbene with the Mn(III) complex.

The mechanism of action of chiral Mn–salen complexes and related metalloporphyrins as homogeneous catalysts has been extensively studied previously.[10] The current view on the nature of the active site focuses on the intermediary oxomanganese(V) species $[salen\text{–}Mn^{V}{=}O]^{+}$ which is suggested to form after addition of PhIO to the Mn(III)–salen complex. Bryliakov *et al.*[31,32] have used EPR to monitor the interaction of PhIO with a Mn(III)–salen complex in solution after addition of PhIO, and observed pronounced changes in the spectrum which they assigned to the formation of a Mn^{III}(salen)(OIPh) adduct. Further work by the same group using ^{1}H NMR suggested the formation of at least three types of manganese species after interaction of the Mn^{III} complex with PhIO. Two relatively inert dimers $[L(salen)Mn^{IV}\text{–}O\text{–}Mn^{IV}(salen)L']^{2+}$ with different axial ligands were identified in addition to an oxomanganese(V) intermediate $[(salen)\text{–}Mn^{V}{=}O]^{+}$. This latter oxomanganese(V) species has been implicated as an important intermediate in the observed enantioselectivities of these Mn–salen type complexes. One proposed epoxidation mechanism involves approach of the alkene to this active species in a *side-on manner*[33,34] and this has been used to account for the high reactivity of (*Z*)-alkenes and the much poorer results obtained with (*E*)-alkenes. For a (*Z*)-alkene, approaching the manganese –oxygen bond from the side permits maximum overlap between the occupied π orbitals of the (*Z*)-alkene and the π antibonding orbitals of the metal-oxo group and this results in a high yield for the epoxide. However, a similar approach of the (*E*)-alkene involves an unfavourable steric interaction between one of the alkene substituents and the ligand. This steric effect leads to lower reactivity and a lower yield of the epoxide product. In our previous study,[20,21] we have shown that lower reactivity for (*E*)-stilbene compared with (*Z*)-stilbene is also observed with the heterogeneous catalyst. The generation of both *cis*- and *trans*-epoxides as primary products from acyclic (*Z*)-alkenes is a common feature of this metal–salen oxo-transfer catalysis[35] and it is attributed to stepwise C–O bond



Scheme 1 Epoxide formation from the radical intermediate.

formation *via* a radical intermediate[36] (Scheme 1). The radical intermediate can either undergo ring closure to give the *cis*-epoxide or rotation followed by ring closure to give the *trans*-epoxide. Retention of configuration arises if C–O bond formation is faster than the rotation process. Recently, Norrby *et al.*[37] have proposed that a manganaoxetane intermediate forms between the alkene and the active species (salen–Mn=O) and this involves a twisted salen ligand. The oxetane intermediate can then rearrange to give the *cis*-epoxide, or homolytic cleavage of the Mn–C bond can lead to radical formation (*cf.* Scheme 1) which can give either the *cis* or *trans* product, as described above. From the results presented in this study, it is clear that, for the homogeneously catalysed reaction, rotation of the radical intermediate is preferred since the more thermodynamically stable *trans*-epoxide is the major product. In the heterogeneously catalysed process, it is apparent that retention of configuration is observed and it is proposed that this is due to restriction of the molecular rotation of the radical intermediate within the mesopores of the Mn-Al-MCM-41 catalyst. To test this further, a series of experiments was designed to investigate the *cis*/*trans* product selectivity of active sites located within the mesopores of the MCM-41 material, compared to the active sites located on the external surface of the crystallites. It is considered that sites located within the mesopores of the crystals (pore size 3.8 nm) would impose more steric hindrance to rotation of the radical intermediate compared with sites on the external surface.

Al-MCM-41 is prepared using an organic template molecule which is located within the mesopores following hydrothermal treatment and helps form the regular mesoporous structure. Prior to use as a catalyst, the template is removed by calcination at 550 °C. To examine the contribution of active sites located on the particle surface, as opposed to those within the mesopores, a catalyst was prepared by Mn-exchange of a non-calcined Al-MCM-41 which gave a sample containing 1% Mn by weight. Prior to use as a catalyst, the sample was degassed *in vacuo* at 100 °C to remove water but not the template. The results for the epoxidation of (*Z*)-stilbene are given in Table 5. No change in enantioselection was observed for the non-calcined catalyst but there was a marked difference in the *cis*:*trans* product ratio with the *trans*-epoxide being preferentially formed. Indeed, the *cis*:*trans* ratio observed is similar to that obtained from the homogeneously catalysed reaction using **6** as catalyst (Table 3). This indicates that Mn–salen immobilised on the external surface of the MCM-41 crystallites behaves in a similar way to the solution complex and there is no additional limitation to rotation in the radical intermediate when the complex is immobilised in this way. To investigate the selectivity of Mn–salen immobilised within the mesopores, a further experiment was conducted. A sample of non-calcined Al-MCM-41 was silanised prior to calcination. In this way, the external surface sites of the Al-MCM-41 were preferentially silylated and were no longer available for ion-exchange.

Table 5 Investigation of silanised catalysts

Catalyst[a]	Reaction time[b]/h	Epoxide yield (%)			Ee *trans* (%)
		Total	*cis*[c]	*trans*[c]	
Calcined	2	69	58	42	70
Non-calcined	4	70	29	71	70
External surface silanised	2	61	44	56	67
Completely silanised	2	0	—	—	—

[a] Calcined = Al-MCM-41 calcined at 550 °C to remove template prior to Mn^{2+}-ion exchange and salen modification; non-calcined = Al-MCM-41 not calcined to remove template prior to Mn^{2+}-ion exchange; external surface silanised = non calcined Al-MCM-41 silanised prior to calcination at 550 °C to remove template; completely silanised = calcined Al-MCM-41 silanised prior to Mn^{2+}-ion exchange. [b] Time for complete conversion of iodosylbenzene. [c] Normalised to 100% yield.

A recent paper by Antochshuk and Jaroniec[38] has indicated that, for the silica only form of MCM-41 (*i.e.* no Al is incorporated into the framework), treatment with trialkyl silanes, together with excess anhydrous pyridine for extended reaction periods (36 h), leads to the removal of the template from the MCM-41 material. In our study, we wish to react the external surface of the MCM-41 crystallites with the silane to ensure that external Al-sites, following calcination, could be covered with silica and, hence, would be unable to provide ion-exchange sites for Mn^{2+} cations in the subsequent preparation step of the catalyst. The effect of silanisation, using a range of silanisation reagents, on the surface area of the Al-MCM-41 sample was investigated and the results are given in Table 6. It is clear that the silanisation treatments used resulted in partial removal of the template surfactant molecules from the mesopores of Al-MCM-41, since the surface area of the material increased from 25 to 130–350 $m^2\ g^{-1}$, depending on the conditions. The surface area of the material following full removal of the template is *ca.* 900 $m^2\ g^{-1}$ and, hence, it can be concluded that this silanisation procedure does lead to some template removal, preferentially from the pore mouth areas, but that *ca.* 60–70% of the template is retained. Hence, following silanisation, the external surface and Al-sites at the pore mouth areas have been

Table 6 Effect of silanisation reagents on Al-MCM-41 [a]

Silanisation reagent	Time/h	Pyridine [b]	Surface area/ $m^2\ g^{-1}$
None	—	—	23
None, calcined	—	—	900
Trimethylchlorosilane + hexamethyldisiloxane	24	—	350
Trimethylchlorosilane	36	—	250
Trimethylchlorosilane	36	✓	139
Hexamethyldisilazane	36	—	179
Hexamethyldisilazane	36	✓	134

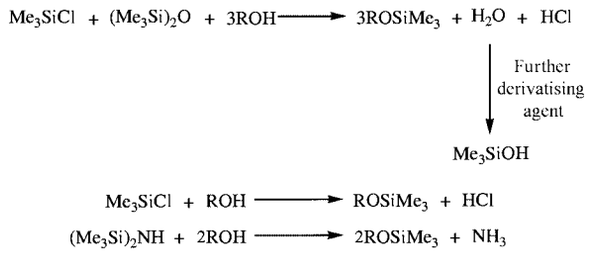
[a] Al-MCM-41 (0.1 g) was refluxed with excess silanising agents for the specified time, with and without the addition of pyridine. [b] Anhydrous pyridine added (25 ml g^{-1} material) after 18 h reflux time.

reacted with silane and these Al are unable to act as sites for subsequent ion-exchange. Subsequent calcination of this silanised material leads to the removal of the remaining template, giving a surface area of *ca.* 900 $m^2\ g^{-1}$, and exposes the Al-sites within the mesopores so that they can act as ion-exchange centres for the immobilisation of Mn^{2+}. It is interesting to note that the removal of the template for Al-MCM-41 is considerably less effective than that reported by Antochshuk and Jaroniec[38] for silica-MCM-41. The presence of aluminium in the MCM-41 framework is clearly influencing the degree of template removal, although there must also be a secondary effect as different silanising agents give slightly different surface areas (Table 6). The primary effect is considered to be due to the ionic interaction between Al and the polar head group of the template molecule.

As both MCM-41 and Al-MCM-41 are prepared from a cationic template, the final material must contain a corresponding anionic moiety. This can be either occluded counter ions from the parent surfactant molecule (in this case Br^-), siloxy species ($(SiO)_3SiO^-$)[39] or tetrahedrally co-ordinated Al species ($(SiO)_4Al^-$).[40] For the first case there is no interaction between the template and the material; therefore these species can easily be removed. In the other cases there is an interaction between template and material and thus the template is more difficult to remove. As the siloxy species is a weaker acid than the aluminosilicate moiety, removal of the template from these sites would be more facile than from the aluminosilicate site. The interaction between material and template needs to be overcome before reaction with the silanising agent occurs (as both the trimethylalkylamine headgroup and the trimethylsilyl derivatising agent have considerable steric bulk).

It is proposed that the treatment of the materials with various silanisation agents can lead to the removal of template molecules from the non-bonded and siloxy-bonded sites (as all template molecules can be removed from pure Si-MCM-41), but not from aluminosilicate sites under the conditions used in this study. It is entirely possible that treatment under elevated temperature and/or longer reaction times may result in complete removal of the template molecule and thus total silanisation of Al-MCM-41.

The secondary process, which is responsible for the variation of surface areas obtained upon silanisation of our Al-MCM-41 samples, is considered to be related to the formation of by-products of the silanisation process as shown in Scheme 2, in particular HCl and trimethylsilanol. Silanisation using the reagents listed in the first equation in Scheme 2 resulted in the greatest template removal, when using the reagents in the third equation, the least amount of template removal was observed. One method of template removal from pure Si-MCM-41 uses acidified ethanol (2 M HCl in ethanol, reflux). Similar compounds are observed as products of the first silanisation procedure described above, namely trimethylsilanol and HCl, which may account for the relatively high levels of template



Scheme 2 Reactions of silanisation agents.

removal. The case in which the next greatest amount of template removal occurs is when HCl is produced as by-product. In this case Me_3SiCl would act as the solvent. Presumably alcohols are better solvents than chlorinated compounds for template removal as dissociation of the alcohol moiety results in the liberation of a proton which may then interact with the anionic moiety on the MCM-41 surface, releasing the template molecule. In the final case using hexamethyldisilazane, no HCl is produced so the template removal is more difficult. Template removal only occurs in this case when the template is displaced by 'Me_3Si^+'.

The role of HCl in the template removal is confirmed by experiments carried out in the presence of pyridine (which is known to catalyse silanisation reactions). Pyridine will react with any HCl present to form the corresponding pyridinium chloride salt, removing any advantage obtained by having the HCl present. This may explain why pyridine is added half way through the silanisation reaction period, rather than at the start of the reaction, in the study of Antochshuk and Jaroniec.[38]

The silanised (using trimethylchlorosilane with hexamethyldisiloxane) calcined sample was Mn-exchanged to give a catalyst, containing 2.1% by weight Mn, in which the Mn was now located only within the mesopores. When used as a catalyst for the epoxidation of (*Z*)-stilbene, no significant effect was observed in the enantioselection of the catalyst but the *cis*:*trans* product ratio was close to unity. This demonstrates that Mn–salen located within the mesopores gives more *cis*-epoxide, indicating that rotation in the radical intermediate (Scheme 1) is hindered within the mesopores of MCM-41. Silanisation of calcined Al-MCM-41 prior to Mn-exchange leads to modification of all the ion-exchange sites and, consequently, the resulting material is inactive as an epoxidation catalyst (Table 5).

It is clear from the data presented in Fig. 1 that the heterogeneously catalysed reaction is markedly different from the homogeneous system with respect to the effect of temperature on enantioselection. In particular, at −10 °C, Mn–salen immobilised on Al-MCM-41 gives the *trans*-epoxide with a very low ee compared to the non-immobilised complex **6**. To investigate this further, we have studied the effect of reaction time on enantioselection, and the data are given in Fig. 3. The homogeneously catalysed reaction shows no change in ee of the *trans*-epoxide with increasing conversion. However, the heterogeneously catalysed reaction shows a marked dependence. At low conversion, *i.e.* 2 min reaction time, the enantioselection at −10 °C is similar to that observed at 25 °C, but it decreases steadily with increasing conversion. Analyses at 2 min reaction time for 25 and 70 °C showed that the enantioselection at low conversion (Table 7) was similar to that at high conversion (Fig. 1) for both temperatures and, hence, the effect was particularly marked at low temperature (*i.e.* −10 °C). However, it must be noted that the immobilised Mn–salen complex always gives lower ee than the homogeneous system (Fig. 1).

Use of PhIO as oxygen donor leads to the formation of PhI as by-product, and this could interact with the Mn-Al-MCM-41 catalyst. Addition of PhI to the homogeneous reaction system did not result in any change in ee or rate of reaction. To investigate the effect of PhI on the heterogeneous

Table 7 Effect of reaction time on enantioselection[a]

Temperature/°C	Ee *trans* (%) 2 Min	Final[b]
−10	65	29
25	71	70
70	57	60

[a] (*Z*)-Stilbene–PhIO–catalyst = 7 : 1 : 0.13, in CH_2Cl_2, catalyst Mn-exchanged Al-MCM-41 containing 2% Mn refluxed with **5** for 24 h. [b] Final reaction times: −10 °C, 6 h; 25 °C, 2 h; 70 °C, 1 h.

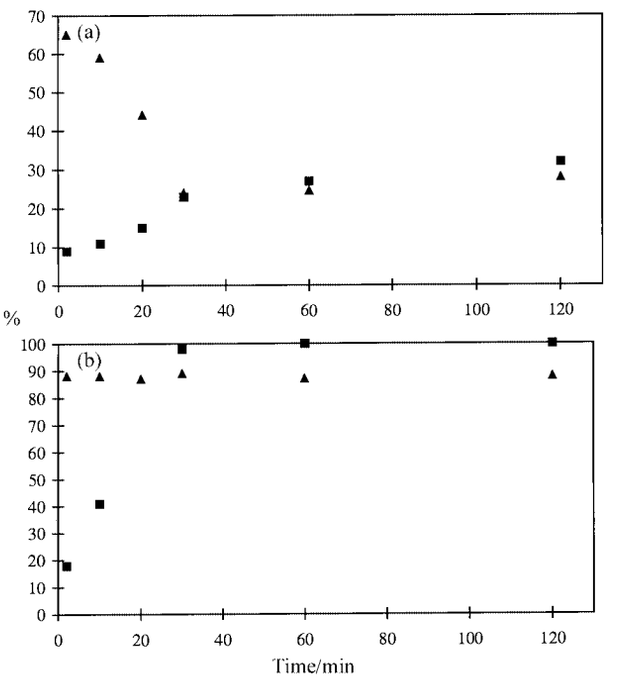


Fig. 3 Effect of reaction time on enantioselectivity at −10 °C (a) heterogeneous catalyst Mn-Al-MCM-41 modified with (*R*,*R*)-(−)-ligand; (b) homogeneous catalyst Mn–salen complex **6**; reaction conditions: substrate L–PhIO–catalyst molar ratio = 7 : 1 : 0.13, in CH_2Cl_2; heterogeneous catalysts contain 0.1 mol ligand per mol Mn. Key: ▲ ee *trans*-epoxide (%), ■ total epoxide yield (%).

catalyst, two further experiments were conducted. First, the effect of PhI addition on the rate of decomposition of PhIO to PhI and O_2 over Mn-exchanged Al-MCM-41 in the absence of (*Z*)-stilbene was studied by monitoring the conversion of PhIO as a function of PhI (Fig. 4). It is apparent that addition of PhI decreases the rate of PhIO decomposition. This is considered to be due to PhI acting as a poison for the active Mn centres. Secondly, a similar experiment was conducted in which PhI was added prior to the addition of PhIO for the heterogeneously catalysed reaction and the results are shown in Table 8. Addition of PhI significantly decreases the rate of reaction, the total yield of epoxide and the ee of the *trans*-epoxide. This confirms that PhI, the degradation product of the oxygen donor, acts as a catalyst poison for the heterogeneous Mn-Al-MCM-41 catalyst and this effect leads to a loss in enantioselection of the catalyst. Poisoning of the catalyst by PhI may also provide a reason why catalyst re-use can be difficult for immobilised chiral Mn–salen catalysts, a feature we have commented upon previously.[20,21] Sherrington,[41] in a recent review, has also commented on the poor catalytic performance of re-used immobilised Mn–salen catalysts and suggests this is due to the fragile nature of the immobilised complex. While this may indeed play a role, since the loss or degradation of the salen ligand can be expected, our study suggests that the effect of poisons may also be significant. The poisoning effect observed with PhI on the heterogeneous catalyst is also manifested in the results presented earlier in this

Table 8 Effect of PhI addition[a]

PhI : PhIO ratio	Reaction time[b]/h	Epoxide yield (%) Total	*cis*[c]	*trans*[c]	Ee *trans* (%)
0	2	63	58	42	70
0.5[d]	6	53	46	54	47

[a] (*Z*)-Stilbene : PhIO : catalyst = 7 : 1 : 0.13, in CH_2Cl_2 at 25 °C, catalyst Mn-exchanged Al-MCM-41 containing 2% Mn refluxed with **5** for 24 h. [b] Time for complete conversion of PhIO to PhI. [c] Normalised to 100% epoxide yield. [d] PhI added to catalyst and stirred in CH_2Cl_2 for 30 min prior to addition of PhIO.

Table 9 Effect of variation in oxygen donor[a]

Oxygen donor	Reaction time[b]/h	Epoxide yield (%) Total	*cis*[c]	*trans*[c]	Ee *trans* (%)
Iodosyl	2	69	58	42	70
4-Nitroiodosylbenzene	48	0	—	—	—
4-Methyliodosyl-benzene	4	54	56	44	69

[a] (*Z*)-Stilbene–oxygen donor–catalyst = 7 : 1 : 0.13, in CH_2Cl_2 at 25 °C, catalyst Mn-exchanged Al-MCM-41 containing 2% Mn refluxed with **5** for 24 h. [b] Time for complete conversion of the iodosylarene to the iodoarene. [c] Normalised for 100% epoxide yield.

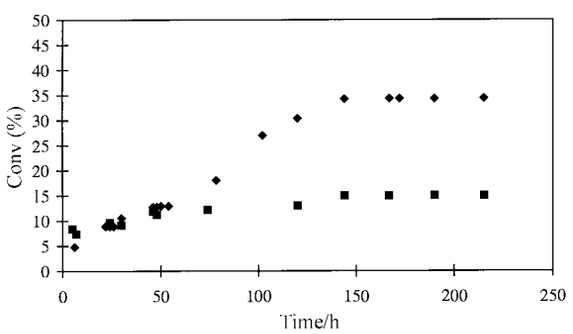


Fig. 4 Effect of PhI addition on PhIO decomposition over Mn-Al-MCM-41 at 25 °C; reaction conditions: (*Z*)-stilbene–PhIO–catalyst molar ratio 7 : 1 : 0.13 in $CHCl_2$. Key: ◆ no PhI addition, ■ PhI added (PhI : PhIO ratio = 0.5).

paper. Increasing the amount of PhIO at fixed (*Z*)-stilbene (Table 3) showed that the total epoxide yield and the *trans*-epoxide ee both decrease as the PhIO/(*Z*)-stilbene ratio is increased and this effect is considered to be due to PhI being adsorbed preferentially on the catalyst. The *cis* : *trans*-epoxide ratio significantly increases at −10 °C, the temperature at which the effect of PhI poisoning appears to be most marked. The increase in the formation of the *cis*-epoxide could be caused by congestion at the active site by PhI which, even in the absence of any specific interaction between PhI and the components of the relevant transition states, would lead to decreased enantioselection and provide an additional barrier to bond rotation and, hence, favour *cis*-epoxide.

The effect of modification of PhIO was studied and the results (Table 9) show that substitution with an electron donating group (4-methyliodosylbenzene) decreased the reaction rate but the results were similar to iodosylbenzene. Interestingly, substitution with an electron withdrawing substituent (4-nitroiodosylbenzene) completely deactivated the oxygen donor.

Experimental

^{1}H NMR spectra were recorded on Bruker AC300 and AMX400 spectrometers, equipped with an X32 computer. Unless otherwise stated chemical shifts for ^{1}H NMR are

recorded in deuteriochloroform. Spectra were recorded on the δ scale and signals are quoted in the form: chemical shift measured in ppm (no. of protons, multiplicity, assignment). EPR spectra were recorded on a Varian E109 X-band spectrometer using 100 KHz field modulation. Flash column chromatography was performed on Merck Kieselgel 60 (230–400 mesh) and analytical TLC on silica gel 60 F-254 plates. Powder X-ray diffraction was performed on an ENRAF Nonius FRS90 Generator with PSD 120 and Cu-Kα source 30 mA, 40 keV. BET analysis was performed on a Micromimetic ASAP 2000. HPLC analysis was performed using a Dynamax SD200 pump equipped with automatic sample injector and UV absorbance detector. Analysis of racemic mixtures was performed using an APEX ODS 5 μm column. The eluent system was acetonitrile–water, 90 : 10. Analysis of chiral compounds was performed using a Pirkle Covalen (*R*,*R*) Whelk-O column and the eluent system was hexane–propan-2-ol, 92 : 8.

Materials

(*Z*)-Stilbene, trimethylsilyl chloride, hexamethyldisiloxane, hexamethyldisilazane, 4-nitroiodobenzene, 4-methyliodobenzene, (*R*,*R*)-(−)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-cyclohexane-1,2-diamine, (*R*,*R*)-(−)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)cyclohexane-1,2-diaminemanganese(III) chloride, manganese(II) acetate, and (diacetoxyiodo)benzene were obtained from Aldrich and used as received. Pyridine was obtained from Fischer, dried over KOH and distilled onto molecular sieves prior to use. Tetramethylammonium silicate solution (25 wt%), tetramethylammonium hydroxide solution (25 wt%) were obtained from Lancaster and used as received. Sodium aluminate was obtained from Hopkin & Williams and used as received. Fumed silica was obtained from BDH and used as received. *n*-Dodecyltrimethylammonium chloride solution was prepared by batch exchange of a 29% by weight aqueous *n*-dodecyltrimethylammonium chloride (40.0 g, BDH) solution in water (11.0 g) and propan-2-ol (28.8 g), with Amberlite IRA-93(OH) standard grade exchange resin (11.8 g, BDH).

Preparation of Al-MCM-41

Al-MCM-41 was prepared according to the method of Kresge *et al.*[42] $C_{12}H_{25}(CH_3)_3NOH/Cl$ solution (61.3 g) was stirred with water (160 g). Sodium aluminate (2.77 g) was added slowly. Fumed silica (16.7 g), tetramethylammonium silicate solution (25 wt%, 46.7 g) and tetramethylammonium hydroxide solution (25 wt%, 8.8 g) were added with stirring. The mixture was heated in an autoclave at 100 °C for 24 h after which the solid material was collected, washed with water and calcined at 550 °C under flowing nitrogen for 4 h and in air for 12 h. Nitrogen adsorption–desorption measurements using the BET method at −178 °C confirmed that this material was mesoporous. Average pore diameter: 38 Å, BET surface area: 900 m^2 g^{-1}. X-Ray powder diffraction patterns of the solid sample gave results in agreement with spectra published in the literature.

Preparation of Mn-Al-MCM-41

Calcined Al-MCM-41 (3 g) was stirred in manganese(II) acetate solution in water (100 ml, 0.2 M) for 24 h. The material was then filtered, washed, dried and then stirred again in a fresh manganese(II) acetate solution for a further 24 h. This process was repeated a further two times. Finally the exchanged material was calcined (550 °C) for 8 h prior to use; Mn content 2.0% by weight.

Silanisation of Al-MCM-41

Silanisation of Al-MCM-41 was carried out according to the method of Beck *et al.*[43] Al-MCM-41 (0.5 g) was refluxed with trimethylchlorosilane (10 g) and hexamethyldisiloxane (15 g) for 16 h with stirring. The product was recovered as a white powder by rotary evaporation, washed with acetone and dried at 25 °C.

Preparation of Mn-Al-MCM-41–salen catalyst

Mn-Al-MCM-41–salen was prepared by refluxing calcined Mn-MCM-41 (0.11 g) with (*R*,*R*)-(−)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)cyclohexane-1,2-diamine (0.03 g) in dichloromethane (4.0 ml) for 24 h. The mixture was cooled to 0 °C, then filtered and washed with dichloromethane and used immediately. This procedure resulted in *ca*. 10% of the chiral salen ligand being incorporated (determined by analysis of the solution following the adsorption step).

Preparation of iodosylbenzene

(Diacetoxyiodo)benzene (16.1 g) was added to aqueous sodium hydroxide (9 g in 75 ml) over a 5 min period. The lumps of solid that formed were macerated for 15 min and the reaction mixture was permitted to stand for an additional 45 min to complete the reaction when a clear solution was obtained. Water (50 ml) was added to precipitate iodosylbenzene as a yellow solid. The solid was then macerated in water (50 ml) and reprecipitated as described before. Final purification was effected by macerating the dried solid in chloroform (75 ml).

Preparation of 4-nitroiodosylbenzene

4-Nitro(diacetoxyiodo)benzene was prepared by the method of McKillop and Kemp.[44] Sodium perborate tetrahydrate (200 mmol, 30 g) was added to a stirred solution of 4-nitroiodobenzene (20 mmol, 5 g) in glacial acetic acid (180 ml). The mixture was stirred (40 °C, 16 h), concentrated to 50% under vacuum and water (100 ml) added. The solid was collected by filtration, washed with water and dried in air. The product, 4-nitro(diacetoxyiodo)benzene, was recrystallised from acetic acid–cyclohexane, 1 : 1, as an orange solid. 4-Nitroiodosylbenzene was prepared from 4-nitro(diacetoxyiodo)benzene by the same procedure as used for the synthesis of iodosylbenzene.

Preparation of 4-methyliodosylbenzene

4-Methyl(diacetoxyiodo)benzene was prepared by the method of Varvoglis.[45] 4-Methyliodobenzene (20 g) was added to a solution of peracetic acid (32% by weight in acetic acid, 190 ml) under reflux. The solution was cooled and water was added and the crystalline product was collected by filtration. The product, 4-methyl(diacetoxyiodo)benzene, was washed with cold water and dried. 4-Methyliodosylbenzene was prepared from 4-methyl(diacetoxyiodo)benzene, by the same procedure as used for the synthesis of iodosylbenzene.

Homogeneous epoxidation

Iodosylbenzene (0.055 g, 0.25 mmol), (*Z*)-stilbene (0.31 ml, 1.75 mmol) and (*R*,*R*)-(−)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)cyclohexane-1,2-diaminemanganese(III) chloride (13 mol%) were stirred in dichloromethane (4.0 ml). Once the reaction was complete, the mixture was filtered through a plug of silica with dichloromethane as eluent. Flash column chromatography (1.5 × 20 cm silica, 30 : 70 dichloromethane–petroleum ether 40–60) gave (*Z*)-stilbene oxide and (*E*)-stilbene oxide as crystalline solids: for (*Z*)-stilbene oxide δ_H (200 MHz, $CDCl_3$) 7.13 (10H, m, Ar-H), 4.32 (2H, s, *cis*-epoxide H); for (*E*)-stilbene oxide δ_H 7.35 (10H, m, Ar-H), 3.85 (2H, s, *trans*-epoxide H).

Heterogeneous epoxidation

Iodosylbenzene (0.055 g, 0.25 mmol), (*Z*)-stilbene (0.31 ml, 1.75 mmol) and Mn-Al-MCM-41–salen catalyst (13 mol%) were stirred in dichloromethane (4.0 ml) at a controlled temperature. The iodosylbenzene was added after the addition of

(*Z*)-stilbene. Once the reaction was complete, the mixture was filtered through a plug of silica with dichloromethane as eluent. Flash column chromatography (1.5 × 20 cm silica, 30 : 70 dichloromethane–petroleum ether 40–60) gave (*Z*)-stilbene oxide and (*E*)-stilbene oxide as crystalline solids.

Conclusions

We have shown that immobilisation of the chiral Mn–salen complex in Al-MCM-41 increases the *cis* : *trans* ratio of the epoxide product when compared to the non-immobilised complex under the same conditions. A non-calcined Al-MCM-41 catalyst has been used to demonstrate that immobilisation of Mn–salen on the external surface of the Al-MCM-41 crystallites gives a catalyst with similar product selectivity and enantioselectivity to the equivalent homogeneous Mn–salen complex, whereas silanisation of the external sites of the Al-MCM-41 catalyst shows that the initial sites have enhanced selectivity to the *cis*-epoxide. This indicates that Mn–salen immobilised within the mesopores of Al-MCM-41 restricts the rotation in the radical intermediate, thereby decreasing the rate of formation of the *trans*-epoxide. Iodobenzene, a by-product formed from the oxygen donor iodosylbenzene, has been shown to act as a catalyst poison leading to a loss in the overall yield of the epoxide product and the ee from the *trans*-epoxide.

Acknowledgements

We thank Synetix, Robinson Bros., the EPSRC and the DTI/LINK programme on asymmetric synthesis, for financial support.

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