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Catalytic asymmetric epoxidation of stilbene using a chiral salen complex immobilized in Mn-exchanged Al-MCM-41

Paola Piaggio,[a] Christopher Langham,[a] Paul McMorn,[a] Donald Bethell,[b] Philip C. Bulman-Page,[c] Frederick E. Hancock,[d] Chris Sly[e] and Graham J. Hutchings *[a]

[a] *Department of Chemistry, PO Box 912, Cardiff University, Cardiff, UK CF10 3TB*
[b] *Department of Chemistry, University of Liverpool, Liverpool, UK L69 3BX*
[c] *Department of Chemistry, Loughborough University, Loughborough, Leicestershire, UK LE11 3TU*
[d] *Synetix, R & T Division, PO Box 1, Billingham, Teeside, UK TS23 1LB*
[e] *Robinson Brothers Ltd., Phoenix Street, West Bromwich, West Midlands, UK B70 0AH*

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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] can be used as an enantioselective heterogeneous epoxidation catalyst using iodosyl benzene as oxygen donor. Epoxidation of (*Z*)- and (*E*)-stilbene is studied in detail and experiments are described that demonstrate that the reaction is wholly catalysed heterogeneously. Similar enantioselectivity is observed for the oxidation of (*Z*)-stilbene to the (*E*)-epoxide using homogeneous (77.5% ee) or heterogeneous (70% ee) catalysts. The effect of temperature, solvents and donor ligands on the yield and enantioselection are discussed.

Introduction

The identification of new catalysts for the synthesis of the building blocks for pharmaceutical and agrochemicals continues to attract public interest. In this respect there is a need for catalysts to be designed which are stable, give high yields of the desired products, and can be readily reused. In particular, there is a need for the design of highly selective asymmetric catalysts. Most of this research concerns homogeneous catalysts, but there is also considerable interest in the identification of heterogeneous asymmetric catalysts, since such catalysts readily overcome the problems typically encountered with homogeneous systems, namely product recovery and catalyst separation. To date, three approaches have been taken in the design of heterogeneous enantioselective catalysts: (i) the use of a chiral support for an achiral metal catalyst,[1] (ii) modification of an achiral heterogeneous catalyst using a chiral cofactor,[2–4] and (iii) the immobilization of a homogeneous catalyst.[5] At present, most success has been achieved with enantioselective hydrogenation catalysts.[2–6] However, one of the biggest challenges remaining is the design of effective heterogeneous enantioselective oxidation catalysts but, to date, this topic is significantly less advanced than the research into enantioselective hydrogenation catalysts. Interest in heterogeneous oxidation catalysts was stimulated by the discovery that the microporous titanium silicalite TS-1 is an effective catalyst for oxidation reactions at 25–60 °C using hydrogen peroxide as oxidant, and this has led to the further observation that a broad range of microporous and mesoporous materials are active oxidation catalysts.[7] To date, these titanium-containing systems have not been successfully modified to act as enantioselective catalysts. In contrast, considerable advances have been made with homogeneous enantioselective epoxidation catalysts.[8–11] Chiral manganese salen complexes have been shown to be very effective asymmetric homogeneous epoxidation catalysts for *cis*-substituted aryl alkenes.[11–13] The identification of heterogeneous counterparts has been somewhat slower, and for manganese(III) complexes a number of approaches have been adopted: (a) support of Jacobsen-type alkene epoxidation catalysts on polymers;[14–16] Canali and Sherrington have reviewed this area;[17] (b) ion exchange of manganese(III) complexes into the intra-crystalline space of zeolites, *e.g.* zeolite Y[18] or mesoporous materials,[19] and (c) encapsulation of manganese(III) complexes within zeolites by synthesis using a "ship in a bottle" methodology.[20] Considerable progress has been made using polymer-supported systems,[14] but the use of inorganic supports has received far less attention. Pre-formed manganese complexes have been ion-exchanged in zeolites, but only using manganese(III) complexed with achiral nitrogen ligands, *e.g.* bipyridyl.[21] Ogunwumi and Bein[20] have demonstrated that the "ship in a bottle" approach can be successfully used to synthesise the asymmetric manganese(III) salen complex inside the cages of the zeolite EMT. Although this method does produce an asymmetric epoxidation catalyst, the pore size of the zeolite can limit the effective range of substrates that can be utilized. In this paper we demonstrate the synthesis of a heterogeneous enantioselective epoxidation catalyst for the larger substrate (*Z*)-stilbene by combining manganese(III) salen with the mesoporous Al-MCM-41. This work extends the methodology previously identified in our studies concerning the enantioselective aziridination of alkenes using Cu^{2+}-exchanged zeolite Y modified with bis(oxazolines).[22] A preliminary account of this work has already appeared.[23]

Results and discussion

Mn-exchanged Al-MCM-41 : salen catalysed epoxidation of (*Z*)-stilbene

One of the most selective catalysts for homogeneous asymmetric epoxidation of alkyl and aryl substituted olefins is a manganese complex of a chiral Schiff base, developed in recent years by Jacobsen *et al.* (Fig. 1).[11,24] Since a heterogeneous reaction would be desirable, an ideal heterogeneous analogue could potentially be obtained from zeolites but, as argued previously, microporous zeolites have pores that are too small to permit diffusion of the chiral Schiff base within the structure. Recently, materials based on amorphous alumino silicates have been synthesized, denoted Al-MCM-41,[25] and these are used in the present study since they permit larger molecules to access the pores.

Table 1 Epoxidation of (*Z*)- and (*E*)-stilbene at 25 °C using Mn–salen catalyst

Entry	Alkene	Catalyst[a]	Time/h	Epoxide yield (%)[b]			ee *trans* (%)[d]
				Total	*cis*[c]	*trans*[c]	
1	(*Z*)-Stilbene	None	2	—	—	—	—
2	(*Z*)-Stilbene	Mn acetate	24	1.5	0	100	—
3	(*Z*)-Stilbene	Mn–salen complex (Fig. 1)	1	86	29	71	77.5
4	(*Z*)-Stilbene	Al-MCM-41	24	0	—	—	—
5	(*Z*)-Stilbene	Mn-Al-MCM-41	2	3	0	100	—
6	(*Z*)-Stilbene	Mn-Al-MCM-41 + ligand[e]	2	69	58	42	70
7	(*Z*)-Stilbene	Mn-Al-MCM-41 + ligand[f]	2	78	62	38	69
8	(*Z*)-Stilbene	Mn-Al-MCM-41 + ligand reused	2	18	61	39	30
9	(*Z*)-Stilbene	Mn-Al-MCM-41 recalcined + ligand	2	52	63	37	54
10	(*E*)-Stilbene	Mn-Al-MCM-41 + ligand[e]	26	35	0	100	25

[a] (*Z*)-Stilbene : oxygen donor : catalyst = 7 : 1 : 0.13. [b] Determined using HPLC, APEX ODS 5μ. [c] Normalized to 100% epoxide yield. [d] Determined using chiral HPLC with Pirkle Covalen (*R*,*R*) Whelk-O column. [e] 1 Equivalent of ligand for every equivalent of Mn refluxed for 1 day, quantity observed 0.1 equivalent of ligand per equivalent of Mn. [f] 3 Equivalents of ligand for every equivalent of Mn refluxed 3 days, quantity observed 0.3 equivalent of ligand per equivalent of Mn.

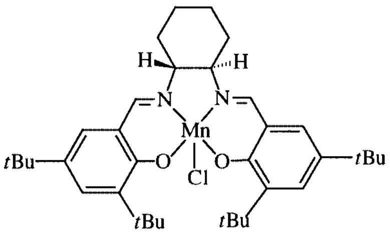

Fig. 1 (*R*,*R*)-(−)-*N*,*N*′-Bis(3,5-di-*tert*-butylsalicylidene)cyclohexane-1,2-diaminomanganese(III) chloride (Jacobsen complex).

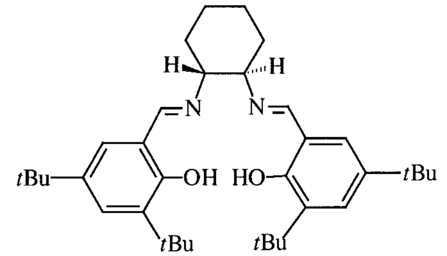

Fig. 2 (*R*,*R*)-(−)-*N*,*N*′-Bis(3,5-di-*tert*-butylsalicylidene)cyclohexane-1,2-diamine (Jacobsen ligand).

For example, bulky substrates and chiral Schiff bases can easily be accommodated. Al-MCM-41 can be readily ion-exchanged to form manganese-exchanged Al-MCM-41, and this material has been selected for the study of the oxidation of (*Z*)-stilbene.

The choice of oxygen donor is of crucial importance. Preferably, environmentally friendly oxidants such as dioxygen or hydrogen peroxide would be best. However, apart from TS-1,[26] microporous and mesoporous silicate-based catalysts are inactive with hydrogen peroxide, and none shows any activity with oxygen. Homogeneous oxidation catalysts based on Mn(III) modified with chiral Schiff bases have utilized sodium hypochlorite or iodosyl mesitylene as oxygen source. Iodosylbenzene has also been successfully used in the epoxidation of alkenes.[27–29] Selection of the oxidant for use with Al-MCM-41 as the catalyst framework must take into account (a) the desirability of a monophasic system, since product recovery and analysis of biphasic liquid systems (*i.e.* two liquid phases in addition to the solid catalyst) can present additional problems, and (b) the necessity that the residue from the oxygen donor does not adsorb strongly onto the catalyst surface, thereby leading to deactivation. For these reasons, we have decided not to use aqueous hydrogen peroxide since, for the oxidation of the substrates of interest, a biphasic system would result. In addition, it is known[30] that water, that would be formed from hydrogen peroxide, can significantly affect the activity of microporous and mesoporous catalysts. We have selected iodosyl benzene as oxygen donor since it does not exhibit these disadvantages.

$Mn(OAc)_2$, in the absence of MCM-41 or salen ligand, is not a particularly active catalyst; only 1.5% yield of the epoxide is formed after reaction of PhIO with a seven-fold excess of (*Z*)-stilbene for 24 h at 25 °C, and only the *trans*-epoxide is formed (entry 2, Table 1). Modification of manganese in solution by the chiral salen ligand [(*R*,*R*)-(−)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)cyclohexane-1,2-diamine] (Fig. 2) as expected leads to a significant rate enhancement, but now the *cis*-epoxide is also formed (entry 3), and the *trans*-epoxide is formed with 77% ee. Interestingly, immobilization of the Mn^{3+} by Al-MCM-41 leads to an increase in reactivity when compared with the non-Mn^{3+} exchanged parent material (*i.e.* Al-MCM-41), and the epoxide is formed with a similar *cis*/*trans* ratio to that seen when using the homogeneously catalysed Mn : salen catalyst (entry 6), whereas non-immobilized Mn^{3+} in the absence of the salen ligand is inactive (entry 2). Analysis by atomic absorption spectrometry of the solution showed that no Mn had been lost during the reaction, and the increased reactivity that is observed suggests that the Al-MCM-41 is occupying part of the manganese coordination sphere and this restricts the *cis*–*trans* interconversion of the alkene. Further modification of the Mn-exchanged-Al-MCM-41 with additional salen leads to a further enhancement in reactivity and in the *cis*/*trans* ratio of the epoxide (entry 7). The *trans*-epoxide is formed with an ee of 70% which is very similar to that observed for the equivalent homogeneous reactions (entry 3).

(*E*)-Stilbene (entry 10) is found to be a significantly less reactive substrate, and the ee of the resulting *trans*-epoxide is significantly decreased. This effect is also observed in homogeneous reactions[12,24,31,32] and it has been argued that the filled π orbitals of an approaching (*Z*)-alkene molecule maximize overlap with the π^* antibonding orbital of the metal-oxo group, enabling the epoxide to be formed in high yield. The approach for a (*E*)-alkene involves an unfavourable steric interaction between one of the alkene substituents and the ligand plane. Because the degree of orbital overlap is now considerably less than that of the (*Z*)-alkene, the yield of epoxide is significantly lower.

The use of Mn-exchanged-Al-MCM-41 : salen catalyst for this epoxidation reaction does not result in the formation of significant levels of by-products, as has been observed when manganese bypyridyls have been used as catalyst;[20] typically only deoxybenzoin is observed at low levels (*ca.* 5–10%, based on iodosylbenzene), although some decomposition of iodosylbenzene is observed (*ca.* 30%).

Table 2 Effect of water on the epoxidation of (*Z*)-stilbene at 25 °C using Mn–salen catalyst

Entry	Catalyst	H_2O (%)	Time/h	Epoxide yield (%)[a] Total	*cis*[b]	*trans*[b]	ee *trans*[c] (%)
11	Mn–salen complex (Fig. 1)	0	1	91.5	29	71	80
12	Mn–salen complex (Fig. 1)	0.5	1	99.8	23.5	76.5	82.3
13	Mn–salen complex (Fig. 1)	3	1	98.6	22.5	77.5	82.5
14	Mn–salen complex (Fig. 1)	10	1	90.9	24.4	75.6	82
15	Mn–Al-MCM-41 + ligand (Fig. 2)[d]	10	4	46.4	58.4	41.6	62
16	Solution[e]	10	2	10.4	0	100	53.2
17	Solution[e]	10	19	71	50	50	53

[a] Determined using HPLC, APEX ODS 5μ. [b] Normalized to 100% epoxide yield. [c] Determined using chiral HPLC Pirkle Covalen (*R*,*R*) Whelk-O column. [d] 1 Equivalent of ligand for every equivalent of Mn refluxed for 1 day. [e] Solution obtained from reaction 15 following filtration to remove solid catalyst.

A further set of experiments was carried out to examine the reusability of the Mn-exchanged-Al-MCM-41 : salen catalyst. Following the reaction, the Mn-exchanged-Al-MCM-41 : salen catalyst was recovered by filtration and both the solid and the solution were retained for further use. The solid was reused as a catalyst with new reagents (entry 8); although the reactivity and enantioselectivity had declined, epoxide was still formed and the *cis*/*trans* ratio was unchanged. Recalcination of the recovered material from this subsequent experiment and addition of new salen ligand essentially restored both the catalytic activity and the enantioselectivity (entry 9). The solution obtained following filtration was also used in a new reaction with the addition of substrate and oxygen donor. No reaction was observed and, furthermore, analysis of the solution using atomic absorption showed that no Mn had leached from the solid catalyst. Since Mn loss cannot be responsible for the loss of activity from the re-used catalyst, it is possible that, during the first reaction, some ligand was lost from the catalyst, leaving fewer active catalytic centres and, hence, a lower activity catalyst. These experiments demonstrate that the reaction occurring with Mn-exchanged-Al-MCM-41 : salen is wholly catalysed heterogeneously.

Effect of water on homogeneously and heterogeneously catalysed epoxidation of (*Z*)-stilbene

A series of experiments was carried out using the soluble Mn–salen complex (Fig. 1) as a catalyst for the epoxidation of (*Z*)-stilbene to examine the effect of water on the reaction (Table 2, entries 11–14). Addition of water has no effect on the homogeneously catalysed reaction apart from a minor effect in the *cis*/*trans* ratio of the epoxide product. At low levels, it appears to lead to a slight rate enhancement. For the heterogeneously catalysed reaction (Table 2, entry 15), it does lead to a decrease in yield compared to the experiment in the absence of water (Table 1, entry 7), but there is very little effect on the *cis*/*trans* ratio or the ee of the epoxide. However, filtration of the reaction mixture following reaction, and re-use of the solution obtained in a fresh experiment, does reveal some activity and enantioselection (Table 2, entries 16–17). In this case, it is proposed that the added water leads to leaching of the Mn–salen complex from the solid catalyst. This provides further evidence that aqueous solvents of hydrogen peroxide as oxygen donor cannot be used with the Mn-exchanged-Al-MCM-41 : salen catalyst.

Ligand accelerating effect of salen

For the homogeneously catalysed reaction, it is already known that the ligand has an accelerating effect on the rate of reaction. Data (Table 1, entries 2–3) show that unmodified Mn is almost inactive compared to modified Mn and that only *trans*-epoxide is formed. In the present study, it is observed that the ligand also has a considerable accelerating effect on the heterogeneously catalysed reaction (entries 5–6, and Fig. 3), the total yield increases significantly and *cis*-epoxide is now formed. Interestingly, the rate of conversion of iodosylbenzene to iodobenzene is also enhanced for the modified heterogeneous catalyst in the absence of the (*Z*)-stilbene substrate (Fig. 4).

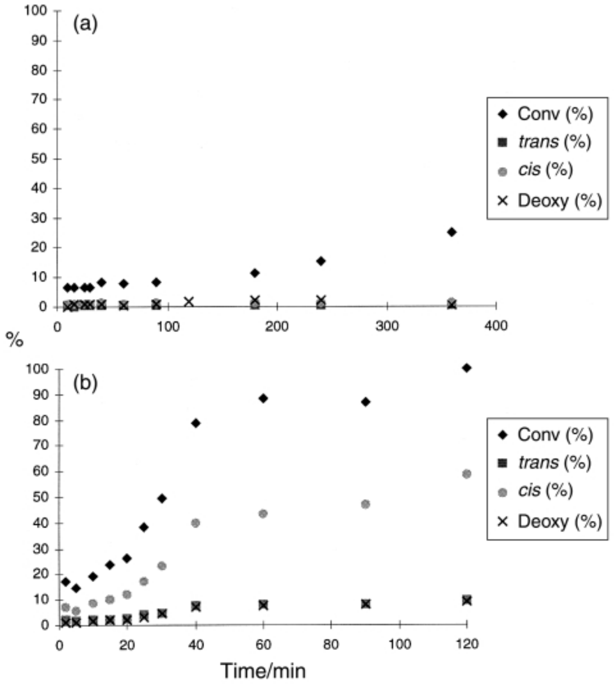

Fig. 3 a) Epoxidation of (*Z*)-stilbene at −10 °C using 7-fold excess of (*Z*)-stilbene and Mn-Al-MCM-41 as catalyst, b) epoxidation of (*Z*)-stilbene at −10 °C using 10-fold excess of (*Z*)-stilbene and Mn-Al-MCM-41 + ligand (Fig. 2) as catalyst. Key: Conv = conversion of PhIO; *trans* = yield of *trans*-epoxide; *cis* = yield of *cis*-epoxide; Deoxy = deoxybenzoin.

Analysis of the filtrate obtained from the catalyst preparation revealed the presence of the salen ligand, showing that the preparation procedure did not enable all the salen ligand to be adsorbed. Two methods of preparation were investigated in which different amounts of the salen ligand were used. When these materials were used as catalysts (Table 1, entries 6, 7), no change in the enantioselectivity is observed, although one catalyst (Table 1, entry 7) containing three times as much salen ligand gave an increased yield. The higher yield of epoxide is consistent with the increased Mn-ligand concentration of the catalyst, and the maintenance of the ee indicates that ee is dependent upon the catalyst/ligand structure within the mesopores and is independent of the Mn-ligand concentration.

Effect of temperature on enantioselectivity

Temperature has an important effect on the enantioselectivity observed for the heterogeneously catalysed reaction. Upon cooling from room temperature or upon heating to 70 °C (Table 3), the enantioselectivity decreases significantly. This effect is markedly different to that observed in the homogeneous reaction,[11] for which the best ee is observed at −10 °C (88%). It is possible that the framework of MCM-41 is responsible for this temperature effect. It has been suggested[33] that the steric constraints of the zeolite pores favour a certain conformation of the metal–salen complex. It is possible that this conformation may be stable at 25 °C in the mesopores of the heterogeneous catalyst. In the homogeneous case, lower temperatures are possibly required to achieve the most selective conformation. This behaviour further emphasizes the differences that exist between the homogeneous and the heterogeneous catalysts.

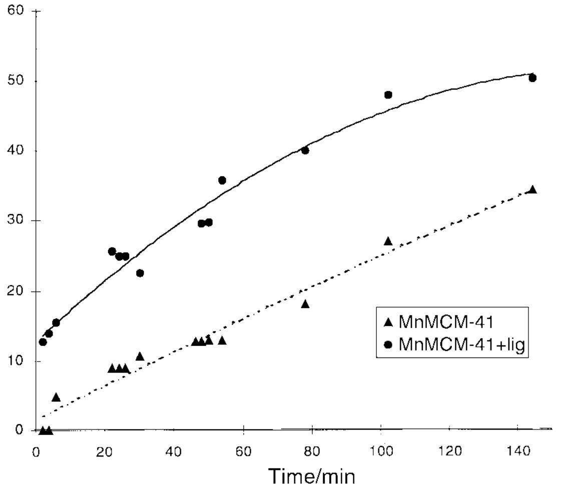

Fig. 4 Decomposition of iodosylbenzene to iodobenzene at −5 °C in dichloromethane. Key ● Mn-exchanged-Al-MCM-41 plus ligand (Fig. 2, one equivalent of ligand for every equivalent of Mn refluxed for 1 day); ▲ Mn-exchanged-Al-MCM-41.

Table 3 Effect of temperature on homogeneously and heterogeneously catalysed epoxidation of (*Z*)-stilbene

			Epoxide yield (%)[b]			
T/°C		Time/h[a]	Total	*cis*[c]	*trans*[c]	ee *trans* (%)[d]
70	Homo	0.5	93.9	36.3	63.7	79.5
	Hetero	1	35	69	31	60
50	Homo	0.5	100	25	75	78
	Hetero	1	65.3	55.6	44.4	62
37	Homo	0.5	100	30	70	78
	Hetero	3	75.8	60	40	64
25	Homo	1	91	29	71	80
	Hetero	2	69	58	42	70
5	Homo	1	100	30	70	86
	Hetero	4	67	80	20	47
−10	Homo	2	100	23	77	88
	Hetero	6	35	85	15	29

[a] Reactions followed until total conversion of iodosylbenzene to iodobenzene. [b] Determined using HPLC, APEX ODS 5μ. [c] Normalized to 100% epoxide yield. [d] Determined using chiral HPLC with Pirkle Covalen (*R*,*R*) Whelk-O column.

As expected, decreasing the temperature results in the reaction becoming slower and more *cis*-epoxide is formed because the radical pathway that leads to the *trans* product is less favoured at low temperature. At 70 °C the epoxide decomposes quite quickly after formation, hence a very low yield (35%) is obtained.

Effect of solvents on enantioselectivity

We have screened a variety of solvents (Table 4) and confirmed that dichloromethane is the most suitable solvent for the heterogeneous system. The considerable decrease of enantioselectivity caused by the use of toluene and hexane as solvents may be due to the polarity of these solvents in comparison with dichloromethane. Acetonitrile and tetrahydrofuran can take part in coordination on the Mn centre, competing with the iodosylbenzene and (*Z*)-stilbene coordination, hence leading to the lower yields observed compared with dichloromethane as solvent.

Effect of donor ligands on enantioselectivity

It has been observed previously[34] in homogeneous systems that addition of donor ligands such as pyridine *N*-oxide or *N*-methylimidazole induces a conformational change on the skeleton of the manganese(III) salen complexes, resulting in enhancement of reaction rate and an improvement in enantioselectivity. We have screened these donor ligands in our heterogeneous system and observed a reduction in both yield and enantioselectivity (Table 5). This observation of different results obtained for heterogeneous and homogeneous reactions suggests that the MCM-41 framework has an inhibiting effect on the coordination of the donor ligand or that the coordination causes some steric impediment around the Mn centre which interferes with the reaction. It also provides further support for our contention that the reaction is catalysed wholly heterogeneously and occurs inside the pores of the MCM-41 material.

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 quoted in the form: chemical shift measured in ppm (no. of protons, multiplicity, assignment).

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 ENRAF Nonius

Table 4 Effect of solvents on the heterogeneously catalysed epoxidation of (*Z*)-stilbene at 25 °C

				Epoxide yield (%)[c]			
Solvent type	Solvent	Time (h)[a]	Conv[b] (%)	Total	*cis*[d]	*trans*[d]	ee *trans* (%)[e]
Non coordinating	DCM	2	100	72	56.0	44.0	63.2
	Toluene	7	82	53.3	85.6	14.4	22
	Hexane	4	100	72.7	90.8	9.2	2
Coordinating	CH_3CN	7	75	56.5	75.6	24.4	23
	THF	4	100	27.6	84.4	15.6	59

[a] Reactions followed until total conversion of iodosylbenzene into iodobenzene. [b] Based on the decomposition of iodosylbenzene to iodobenzene. [c] Determined using HPLC, APEX ODS 5μ. [d] Normalized to 100% epoxide yield. [e] Determined using chiral HPLC with Pirkle Covalen (*R*,*R*) Whelk-O column.

Table 5 Effect of donor ligands on the heterogeneously catalysed epoxidation of (*Z*)-stilbene at 25 °C

			Epoxide yield (%)[c]			ee
Donor ligand	Time/h[a]	Conv[b]	Total	*cis*[d]	*trans*[d]	*trans* (%)[e]
None	2	100	72	56	44	63
Pyridine *N*-oxide	4	100	62	68	32	63
N-Methyl-imidazole	3	100	50	77	23	8

[a] Reactions followed until total conversion of iodosylbenzene to iodobenzene. [b] Based on the decomposition of iodosylbenzene to iodobenzene. [c] Determined using HPLC, APEX ODS 5μ. [d] Normalized to 100% epoxide yield. [e] Determined using chiral HPLC with Pirkle Covalen (*R*,*R*) Whelk-O column.

RFS90 Generator with PSD 120 and CuKα 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 5μ 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–isopropanol = 92 : 8.

Materials

(*Z*)-Stilbene, (*E*)-stilbene, (*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-diaminomanganese(III) chloride, manganese(II) acetate and iodobenzene diacetate were obtained from Aldrich and used as received. Tetramethylammonium silicate solution (25wt%), tetramethylammonium hydroxide solution (25wt%) were obtained from Lancaster and used as received. Sodium aluminate was obtained from Hopkin & Williams and used as received. Silica fumed 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.*[35] $C_{12}H_{25}(CH_3)_3NOH/Cl$ solution (61.3 g) was stirred with water (160 g). Sodium aluminate (2.77 g) was added slowly. Silica fumed (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: 570 $m^2\ g^{-1}$. 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 zeolite was calcined (550 °C) for eight hours prior to use; Mn content 2.0% by weight.

Preparation of Mn-Al-MCM-41 : salen catalyst (10% modified)

Mn-Al-MCM-41 : salen was prepared by refluxing calcined Mn-Al-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 10% of the chiral salen ligand being incorporated (determined by analysis of the solution following the adsorption step).

Preparation of Mn-Al-MCM-41 : salen catalyst (30% modified)

Mn-Al-MCM-41 : salen was prepared by refluxing calcined Mn-Al-MCM-41 (0.11 g) with (*R*,*R*)-(−)-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)cyclohexane-1,2-diamine (0.09 g) in dichloromethane (4.0 ml) for 72 h. The mixture was cooled to 0 °C, filtered and washed with dichloromethane and used immediately. This procedure resulted in 30% of the chiral salen ligand being incorporated (determined by analysis of the solution following the adsorption step).

Preparation of iodosylbenzene

Iodobenzene diacetate (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. 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).

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-diaminomanganese(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. 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).

Conclusions

We have shown that Mn-exchanged-Al-MCM-41 when modified by a chiral salen ligand can be an effective enantioselective heterogeneous epoxidation catalyst, and the results presented in this paper extend the generality of the methodology described in our earlier studies of asymmetric enantioselective aziridination using Cu^{2+}-exchanged zeolites.[21] Furthermore, we have shown that increasing the proportion of the salen ligand results in a higher yield of products. We have also illustrated that both the reaction temperature and choice of solvent can have an important effect on the observed enantioselectivity. Similar enantioselectivity is observed for the oxidation of (*Z*)-stilbene to the *trans*-epoxide using homogeneous (77.5% ee) and heterogeneous (70% ee) catalysts. We consider that the approach described for catalyst design, *i.e.* the modification of cations ion-exchanged into microporous or mesoporous materials, may have general applicability and will be of value in the design of improved enantioselective heterogeneous catalysts.

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