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Novel Chiral Sulphonato-Salen-Manganese(III)-Pillared Hydrotalcite Catalysts for the Asymmetric Epoxidation of Styrenes and Cyclic Alkenes

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Abstract: A novel chiral sulphonato-salen-manganese (III) complex has been prepared and intercalated into a Zn-Al layered-double hydroxide (LDH) structure. The resulting catalyst was found to be highly active and enantioselective in the epoxidation of various styrenes and cyclic alkenes when using a combination of pivalaldehyde and molecular oxygen at atmospheric pressure and room temperature. At 94% conversion, 1-methyl-1-cyclohexene could be converted to epoxide with 68% ee and 90% selectivity with a turnover frequency (TOF) of 234 h^{-1}, whereas 4-methylstyrene was converted with 62% ee and 70% selectivity with a TOF of 327 h^{-1}. In the case of styrenes and cyclic alkenes, TOF decreased as follows: α-methylstyrene > 4-methylstyrene > styrene and 1-methyl-1-cyclohexene > 1-phenyl-1-cyclohexene > cyclohexene. The catalyst could be recycled without detectable loss of efficiency.

Keywords: asymmetric epoxidation; chiral salen-manganese(III); heterogeneous catalysis; immobilization; LDH host catalyst

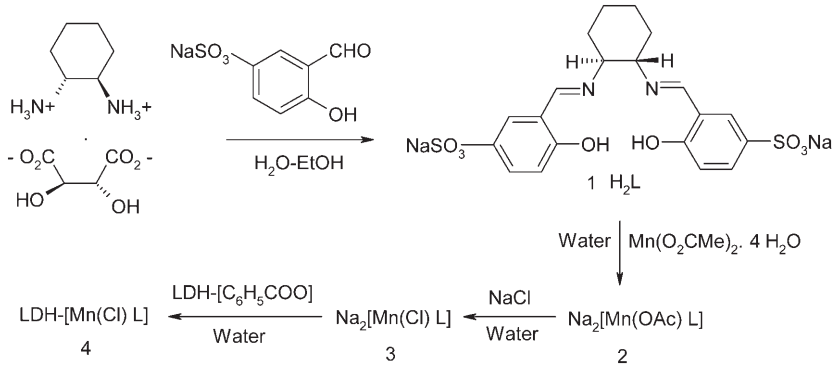
Introduction

Epoxides are important intermediates for the synthesis of complex molecules which find use in fine chemical synthesis. Asymmetric epoxidation of prochiral alkenes presents a powerful strategy for the synthesis of enantiomerically enriched epoxides. In the past two decades there has been great progress in catalytic asymmetric alkene epoxidation. Important contributions have been made using Sharpless[1] and Jacobsen/Katsuki[2–4] systems. Chiral salen-Mn(III) complexes (Jacobsen's catalyst) show high enantioselectivities in the epoxidation of unfunctionalised alkenes under homogenous conditions.[5] Despite high activity, selectivity and chiral induction, this system has several disadvantages including the use of sodium hypochlorite as oxidant, use of chlorinated solvents and the difficulty in recovering the catalyst after use. Cavazzini et al.[6,7] reported that sterically hindered chiral salen-Mn(III) complexes containing long perfluoroalkyl substituents showed similar ee and yield using certain alkenes (indene, 1-methylindene, 1-methylcyclohexene, triphenylethylene, benzosuberene and 1,2-dihydronaphthalene) employing fluorous biphasic conditions under equivalent oxidizing conditions using PhIO/pyridine *N*-oxide when compared with standard homogeneous Mn-salen complexes. The advantage was that the catalysts could be readily recovered from the fluorous layer by simple phase separation techniques at room temperature.[6,7] Ease of separation of the catalyst when it is in a different phase from the reactants/products is also a driver for the heterogenisation of such a system. Various degrees of success have been achieved by attaching the active chiral salen system to zeolites,[8] to polystyrene and polymethacrylate resin (polymer supported),[9] to silica *via* chloropropyl spacers, metallated with manganese[10] and using organo-functionalised mesoporous materials[11] as well as in the subsequent testing of the anchored systems in the epoxidation of alkenes. Kureshy et al.[12] reported on dicationic chiral Mn (III) complexes immobilised between the layers of montmorillonite clay. Subsequent testing of their catalyst in the epoxidation of non-functionalised alkenes using NaOCl as oxidant gave a higher ee for certain alkenes than that found under homogeneous conditions. Recently, Li and co-workers[13,14] demonstrated that chiral salen-Mn(III) catalyst when axially immobilised into MCM-41 through complexation of the manganese *via* the oxygen atoms of the phenoxy groups[13] produced epoxide with 72% ee, whereas the same complex immobilised *via* a phenylsulphonic group[14] gave a slightly higher ee value for the epoxidation of α-methylstyrene. These phenoxy or phenylsulphonic group-anchored catalysts showed significantly higher % ee than the homogenous analogues (56% ee) for α-methylstyrene epoxidation.[13,14]

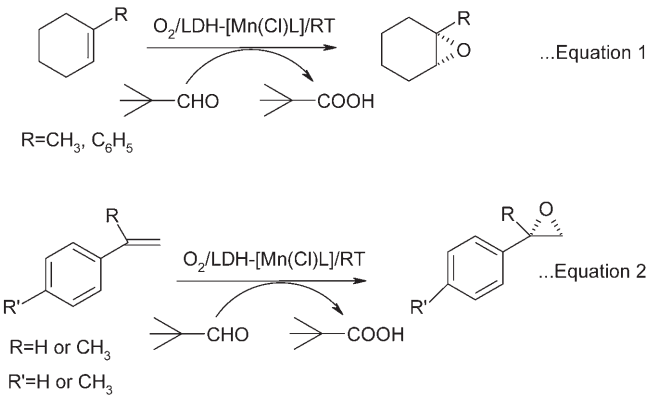
Hydrotalcites, due to their high surface area, homogeneous cation site distribution, basicity and anion exchange capacity, find use in many catalytic applications. Examples of these include catalysed reactions such as Knovenagel,[15] Micheal,[16] Claisen–Schmidt,[17] aldolisations,[18] and in hydrogenation of aromatics as well as in selective oxidation reactions[19] and in the Baeyer–Villiger oxidation of ketones.[20] Recent advances in the pillaring of hydrotalcite by polyoxometallate anions have demonstrated that these materials may exhibit sufficiently large gallery heights to allow catalytic oxidation of relatively large organic compounds[21] including the shape-selective epoxidation of alkenes by changing the size of intercalating species.[22] A tungstate-exchanged, layered double hydroxide was found to show excellent catalytic activity in oxidative bromination and bromide-assisted epoxidation reactions and displayed over 100 times greater activity than its homogeneous analogue.[23] LDH-OsO_4 catalysts have been shown to display good performance in the asymmetric dihydroxylation of olefins.[24] It was recently reported[25] that the chiral sulphonato-salen-manganese(III) complex, Na_2[Mn(Cl)salen], intercalated into a Zn^{II}-Al^{III} layered double hydroxide showed high conversion, selectivity and de in the oxidation of R-(+)-limonene using 75–150 psi of molecular oxygen and pivalaldehyde as sacrificial aldehyde. Later it was shown that this LDH-[Mn(Cl)salen] catalyst[26,27] showed higher conversion, selectivity and de % for R-(+)-limonene and (−)-α-pinene epoxidation under atmospheric pressure of air or dioxygen, compared with published data[28] for other heterogenised Mn-salen catalysts. The catalytic activities and mechanism of the epoxidation of alkenes by LDH-[Mn(Cl)salen] catalyst along with the preparation of other new layered double hydroxide containing salen-metal complexes are currently being pursued to develop a better understanding of the parameters influencing the selectivity of the oxidation products.[29] Although the system described in the present work makes effective use of the sacrificial aldehyde (2:1 molar ratio with substrate) and *in situ* preparation of the peracid is a distinct advantage over the use of externally produced oxidant, ideal methodologies would be based upon the direct use of oxygen or air as oxidant. The present paper deals with the synthesis of a new LDH, $[Zn_{2.15}Al_{0.86}(OH)_{6.02}][Mn(Cl)salen]_{0.19}[C_6H_5COO]_{0.48}\cdot 2\,H_2O$ as well as a study of its performance as a heterogeneous catalyst in the epoxidation of α-methylstyrene, 4-methylstyrene, styrene, 1-methyl-1-cyclohexene, 1-phenyl-1-cyclohexene and cyclohexene using a combination of pivalaldehyde/molecular oxygen at atmospheric pressure as oxidant. Intercalated systems containing chiral salen-manganese(III) complexes for the epoxidation of these molecules have not been previously reported.

Results and Discussion

The preparation of chiral (sulphonato)-manganese(III) and its LDH compound LDH-[Mn(Cl)salen], is outlined in Scheme 1. The chiral Schiff base ligand (abbreviated as **1**; Scheme 1) was prepared by refluxing two equivalents of sodium salicylaldehyde-5-sulphonate and (*R,R*)-1,2-diammoniumcyclohexane mono-(+)-tartrate in a water-ethanol medium. In aqueous solution, the chiral salen ligand, **1**, instantly reacts with manganese(II) acetate tetrahydrate to produce the dianionic compound, Na_2[Mn(OAc)salen] (**2**) in 95% yield. The acetyl ligand in **2** was readily replaced by chloride at room temperature by reaction with NaCl solution to give **3** with good yield (97%). The $[Mn(Cl)salen]^{2-}$ ion was intercalated into the zinc(II)-aluminium(III) layered double hydroxide at room temperature by reaction in aqueous medium between LDH-[C_6H_5COO] and $[Mn(Cl)salen]^{2-}$, by ion exchange of the benzoate ion. The apparent equilibrium constant for the exchange process was calculated as 0.0461 at 298 K. The $[Mn(Cl)salen]^{2-}$ and LDH-[Mn(Cl)salen] (**4**) were characterised by FTIR, TGA, UV-visible, X-ray powder diffraction and elemental analysis.[30] The X-ray powder diffraction patterns of LDH-[C_6H_5COO] and LDH-[Mn(Cl)salen] showed that the basal spacing of the LDH was increased from 15.22 to 18.78 Å following the exchange process. The gallery height of the catalyst



Scheme 1. Preparation of chiral sulphonato-manganese (III) and the LDH-hosted catalyst.



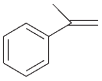
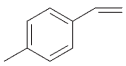
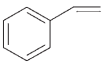
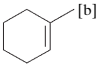
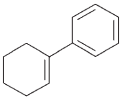
Scheme 2. LDH-hosted Mn-salen-catalysed epoxidation of cyclic alkenes and styrenes in the presence of pivalaldehyde.

is 14.1 Å when the thickness of the brucite layers (4.7 Å) was subtracted. Similarity between the FTIR bands and intensities in the free $[Mn(Cl)salen]^{2-}$ and LDH-[Mn(Cl)salen] compounds, and in particular, the presence of bands at 1116 and 1032 cm^{-1} due to vibrations of the sulphonato group and at 573 cm^{-1} for ν(Mn–O) of the intercalated catalyst **4**, qualitatively confirm the presence of the $[Mn(Cl)salen]^{2-}$ compound in the layered double hydroxide. Elemental analysis of LDH-[Mn(Cl)salen] is consistent with the unit formula $[Zn_{2.15}Al_{0.86}(OH)_{6.02}][Mn(Cl)salen]_{0.19}[C_6H_5COO]_{0.48}\cdot 2\,H_2O$. TGA profiles for $[Mn(Cl)salen]^{2-}$ and LDH-[Mn(Cl)salen] also provide supporting evidence for the successful incorporation of the complex into the LDH-host.[27] The UV-visible (nujol mull) spectrum of the catalyst showed similar features as the free complex, indicating that during intercalation, no change in the local environment of the manganese(III) coordination centre took place.

The epoxidation of α-methylstyrene, 4-methylstyrene, styrene, 1-methyl-1-cyclohexene, 1-phenyl-1-cyclohexene and cyclohexene were studied over the LDH-[Mn(Cl)salen catalyst] at room temperature in the presence of dioxygen and pivalaldehyde using toluene as solvent. The reactions are expressed by Eqs. (1) and (2) (Scheme 2) and the results summarised in Tables 1–3. An example of the reaction profile is shown in Figure 1 which shows the conversion of 4-methylstyrene and selectivity to epoxide. Results indicate that the selectivity to epoxide remained fairly constant at *ca.* 70% even as the substrate underwent conversion in the range of 70 to 90% conversion. During this period, the ee remained constant also at 62% (not shown).

Blank tests under identical reaction conditions revealed that no epoxide was formed using α-methylstyrene, 4-methylstyrene, styrene, 1-methyl-1-cyclohexene and 1-phenyl-1-cyclohexene either when catalyst was absent or when LDH-$[C_6H_5COO]$ alone was added. Cyclohexene was the one exception, being oxidized very slowly (5.5% conversion) after 6 h by dioxygen in the absence of catalysts but under otherwise identical reaction conditions.

Table 1. Epoxidation[a] of α-methylstyrene, 4-methylstyrene, styrene, 1-methyl-1- cyclohexene, 1-phenyl-1-cyclohexene and cyclohexene.

Alkene	Time [h]	Conversion [%]	Epoxide selectivity [%]	ee [%]	TOF[c]
	2.5	91	70	28[d]	360.2
	3.0	94	70	62[d]	327.1
	6.0	71	88	18[e]	121.8
 [b]	4.0	94	90	68[d]	234.2
	6.0	93	86	27	165.0
	6.0	84.0	74	NC[f]	121.2

[a] *Reaction conditions: ca.* 1 mmol, 2 mmol pivalaldehyde, 10 mL toluene, 0.05 g catalyst, 14.5 psi molecular oxygen at 298 K.
[b] Also performed at 358 K, 2 h reaction time and 100 psi dioxygen: conversion, 100%; selectivity, 81%; ee, 67%.
[c] Turnover frequency calculated by the expression [mol product/h^{-1}]/[mol metal catalyst].
[d] Not determined.
[e] Epoxide configuration *S*.
[f] NC, achiral.

Table 2. Performance of reused catalyst in the epoxidation[a] of α-methylstyrene, 4-methylstyrene and styrene.

Run	Alkene	Time [h]	Conversion [%]	Epoxide selectivity [%]	ee [%]
1	α-Methylstyrene	2.5	91	70	28
2	α-Methylstyrene	2.5	91	69	27
3	α-Methylstyrene	2.5	90	69	27
1	4-Methylstyrene	6.0	94	70	62
2	4-Methylstyrene	6.0	95	71	61
3	4-Methylstyrene	6.0	93	70	62
1	Styrene	3.0	71	88	18
2	Styrene	3.0	70	88	18
3	Styrene	3.0	70	87	18

[a] *Reaction conditions: ca.* 1 mmol, 2 mmol pivalaldehyde, 10 mL toluene, 0.05 g catalyst, 14.5 psi molecular oxygen at 298 K.

Table 3. Performance of reused catalyst in the epoxidation[a] of 1-methyl-1-cyclohexene, 1-phenyl-1-cyclohexene and cyclohexene.

Run	Alkene	Time [h]	Conversion [%]	Epoxide selectivity [%]	ee [%]
1	1-Methyl-1-cyclohexene	4.0	94	90	68
2	1-Methyl-1-cyclohexene	4.0	93	89	67
3	1-Methyl-1-cyclohexene	4.0	93	90	67
1	1-Phenyl-1-cyclohexene	6.0	93	86	27
2	1-Phenyl-1-cyclohexene	6.0	93	86	26
1	Cyclohexene	6.0	84	74	–
2	Cyclohexene	6.0	83	74	–
3	Cyclohexene	6.0	83	73	–

[a] *Reaction conditions: ca.* 1 mmol, 2 mmol pivalaldehyde, 10 mL toluene, 0.05 g catalyst, 14.5 psi molecular oxygen at 298 K.

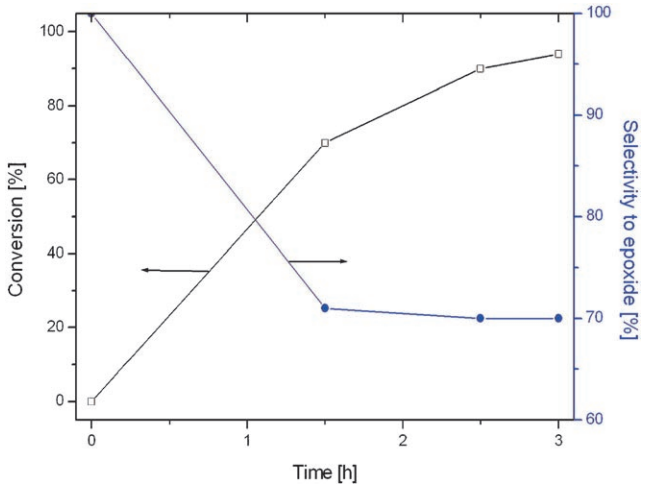


Figure 1. Conversion of 4-methylstyrene and selectivity to epoxide as a function of time at 298 K, 14.5 psi oxygen pressure.

The asymmetric epoxidation of 1-methyl-1-cyclohexene was tested using LDH-[Mn(Cl)salen] catalyst, at atmospheric pressure of dioxygen and at 298 K as well as at a higher pressure (100 psi) and temperature (358 K). Although at higher temperature and pressure the reaction rate was increased, the overall yield of epoxide was only slightly affected as a result of the reduced selectivity whereas the ee was effectively the same under both sets of conditions. The reaction profile for 1-methyl-1-cyclohexene as a function of time is shown in Figure 2. Between 60 and 95% conversion, the selectivity to epoxide remained fairly constant dropping from 92 to 90%. The ee was also only marginally affected with a drop from 70 to 68% over this same conversion range (not shown). The presence of the methyl group in 1-methyl-1-cyclohexene was significant in terms of influencing both activity and selectivity as shown by comparing results with those for cyclohexene. Under identical reaction conditions (298 K and 14.5 psi of molecular oxygen), epoxidation of cyclohexene gave a TOF that was almost half the magnitude while epoxide selectivity was reduced from 90 to 74% (Table 1). However, when compared in the asymmetric epoxidation of 1-methyl-1-cyclohexene and 1-phenyl-1-cyclohexene at atmospheric pressure of dioxygen and at 298 K, the former afforded much higher enantiomeric excess and TOF than the latter (Table 1) although no significant loss in epoxide selectivity was found. The reason for this unexpected negative effect on ee in case of 1-phenyl-1-cyclohexene is unclear at present. The fact that the TOF for the bulky, phenyl-substituted cyclohexene was greater that the cyclohexene itself, suggests that mass transport did not dictate the relative rates of reaction shown in Table 1 and Figure 1.

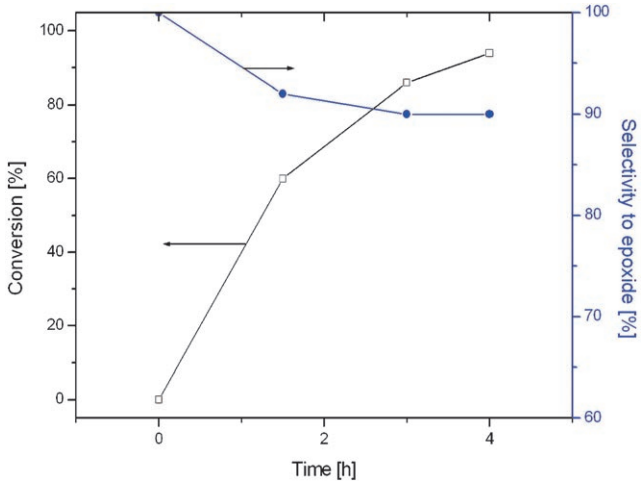


Figure 2. Conversion of 1-methyl-1-cyclohexene and selectivity to epoxide as a function of time at 298 K and 14.5 psi oxygen pressure.

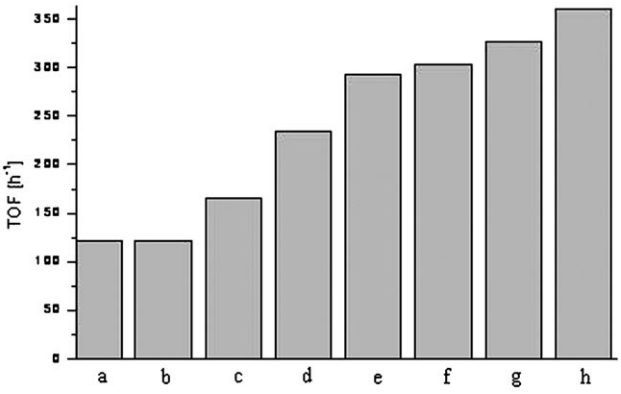


Figure 3. Comparison of TOF (h^{-1}) of: (a) cyclohexene, (b) styrene, (c) 1-phenyl-1-cyclohexene, (d) 1-methyl-1-cyclohexene, (e) *R*-(+)-limonene, (f) (−)-α-pinene, (g) 4-methylstyrene, and (h) α-methylstyrene, over LDH hosted Mn-salen catalyst.

The epoxidation of styrenes was carried out under the identical conditions as for the cyclic alkenes. Among the three substituted styrenes, and in terms of the enantiomeric excess, 4-methylstyrene produced the best results giving epoxide with 62% ee compared to 28 and 18% for α-methylstyrene and styrene, respectively. In terms of double bond activation, methyl substitution either in the *para* (4) or α-positions both led to greater reaction rates. The turnover frequency (TOF) was increased as follows: styrene < 4-methylstyrene < α-methylstyrene.

A comparison of TOF is shown in Figure 3 for the styrenes and cyclic alkenes. For the cyclic alkenes, reaction rate could also be increased by methyl substitution as indicated in Figure 3 where the TOF was increased in the order cyclohexene < 1-phenyl-1-cyclohexene < 1-methyl-1-cyclohexene. The relative TOF of the LDH catalyst in the epoxidation of styrenes and cyclic alkenes showed that the catalytic activity was clearly dependent on the nature of the substrate. It is interesting to note that the styrene (external double bond) and cyclohexene (internal double bond) showed almost the same TOF under identical conditions (Table 1). However, when both functional groups were present such as in *R*-(+)-limonene, the internal double bond was selectively epoxidised,[26,27] indicating that the rate of external double bond epoxidation was increased by the phenyl group with respect to a cyclohexene ring. The catalytic activity of styrene (external double bond) and nitrochromene (internal double bond) using an analogue of Jacobsen's catalyst under homogeneous conditions[31] showed that styrene found much lower TOF than nitrochromene, giving TOFs of 3 and 198 h^{-1} for styrene and nitrochromene, respectively. Again, this illustrates the importance of the substituent groups in activating the alkene function.

Despite the similar reactivity of styrene and cyclohexene, higher TOFs were obtained for methyl-substituted styrenes than for methyl-substituted cyclic alkenes. It was recently shown that α-pinene showed a slightly higher TOF than *R*-(+)-limonene [27] under identical reaction conditions as used for styrenes and cyclic alkenes (Figure 3). The TOF followed the order: cyclohexene = styrene < 1-phenyl-1-cyclohexene < 1-methyl-1-cyclohexene < *R*-(+)-limonene < α-pinene < 4-methylstyrene < α-methylstyrene. The results indicate that the electron-donating methyl group when directly bonded to the alkene functionality, or located in a position which would lead to ring activation, significantly enhances the nucleophilicity of the double bond, thereby increasing the rate of epoxidation.

While using relatively simple, methyl-substituted styrenes and cyclic alkenes, it is possible to assume that steric factors, or rather differences in steric factors as a consequence of major structural dissimilarities, are not responsible for the range of substrate activities and that electronic effects are largely responsible for the range of TOFs observed. However, in terms of ee, it is expected that the structure of the substrate molecule in the vicinity of the alkene double bond will be largely responsible for dictating the chirality of the resulting product. The nature of the bulky ligand groups surrounding the catalyst active centre is also expected to play a major role as summarised in literature findings as follows.

The analogue of Jacobsen's catalyst lacking the bulky *tert*-butyl ligands in the 3 and 5 positions on the phenyl unit, under homogeneous and heterogeneous (encapsulated in zeolite Y) forms, using NaOCl as oxidant at low temperature (at 5 °C), and using 1-methyl-1-cyclohexene and styrene, as substrates gave very poor enantiomeric excess and a very low conversion in the case of 1-methyl-1-cyclohexene.[8] The sterically hindered long perfluoroalkyl-substituted salen-Mn(III) catalyst gave 58% ee at 100% conversion at 100 °C using PhIO/pyridine *N*-oxide in the epoxidation of 1-methyl-1-cyclohex-

ene in the homogeneous phase.[6,7] Another report found that the salen-Mn(III) complexes supported on amorphous silica or MCM-41, using 1-phenylcyclohex-1-ene gave epoxide with 84% ee, when the 3,5-positions of the salicyl phenyl ring of the salen ligand were substituted by *tert*-butyl groups,[32] whereas the enantioselectivity was reduced from 84% to 34%, when the *tert*-butyl group at the 3-position was absent from the phenyl ring of the salen ligand, although electronic modification may play a role in addition to any steric effects.[32] Salen-Mn(III) complexes supported on amorphous silica or MCM-41 catalysts were less effective in the case of styrene, with an ee and epoxide yield of 30% and 70%, respectively.[32] Chiral salen-Mn(III) catalyst when axially immobilised into MCM-41 *via* either phenoxy[13] or phenylsulphonic group[14] showed higher ee % than the homogeneous counterparts for the epoxidation of α-methylstyrene.

In most cases, the enantioselectivity of immobilized salen-Mn(III) catalysts is lower than their homogeneous counterparts. Some of these immobilized catalysts exhibit higher ee values than in the case of their homogeneous counterparts.[12–14,33] The spatial effect including the surface effect originating from the supports as well as the immobilisation modes are considered to be the main reason for the increase in ee values.[13,14,34] We have shown[25–27] that the sulphonato-chiral Mn(III) complex in Zn(II)/Al(III) LDH gave higher de % in the stereoselective epoxidation of *R*-(+)-limonene and α-pinene than the results previously reported for salen-Mn(III). The origin of the high ee of some styrenes and cyclic alkenes using the present LDH hosted catalyst may be associated with the attachment of the salen-Mn(III) complex within the layered double hydroxide *via* the sulphonato group and also potentially, on the presence of positive charges in the layered host along with an appropriate gallery height.

A comparison of some of the better published data for epoxidation of α-methylstyrene, 4-methylstyrene, styrene, 1-methyl-1-cyclohexene, 1-phenyl-1-cyclohexene and cyclohexene compared with that obtained using LDH-[Mn(Cl)salen], is shown in Figure 4. The comparison shows that the modified Jacobsen's catalyst within the LDH host is highly active in non-chlorinated solvent (toluene) and using dioxygen in combination with pivaldehyde as oxidant in the asymmetric epoxidation of 1-methyl-1-cyclohexene, and found to produce the epoxide with slightly lower yield but higher ee % than that reported for perfluoroalkyl-substituted salen-Mn(III) under fluorous biphasic conditions.[6] For the same reaction, the present LDH-based catalyst gave much higher conversion, selectivity and ee than reported for zeolite entrapped Mn-salen[8] where dichloromethane was used as solvent and NaOCl as oxidant. The phenyl-substituted cyclic alkene, 1-phenyl-1-cyclohexene, is a relatively poor substrate (in ee %), and gave much lower ee than previously reported for MCM-41-supported salen-Mn(III).[32] However, the yield of epoxide was much higher here than previously reported.[32] The LDH-[Mn(Cl)salen] catalyst gave a much higher yield of epoxide but with a similar ee for styrene epoxidation as reported for zeolite-entrapped Mn-salen.[8] In the case of α-methylstyrene, salen-Mn(III) when axially immobilised into MCM-41 *via* a phenylsulphonic group[14] gave a much higher ee and yield of epoxide than LDH-hosted catalyst. While the % ee values obtained are very respectable, further modifications to the system are being made which will hopefully yield further improvements.

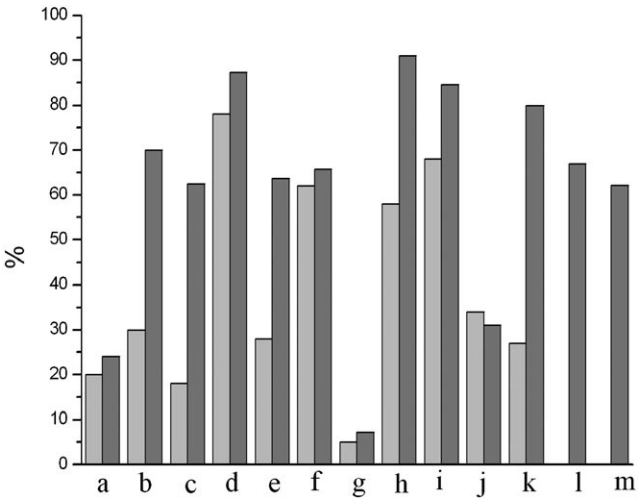


Figure 4. Comparison of ee (light shading) and yield (dark shading) of epoxide (%) of styrene over (a) zeolite-immobilized,[8] (b) MCM-41-supported,[32] (c) LDH-hosted, and α-methylstyrene over (d) MCM-41 *via* phenylsulphonic group,[14] (e) LDH-hosted, and for 4-methylstyrene (f) LDH-hosted, and 1-methyl-1-cyclohexene over (g) zeolite-immobilized,[8] (h) perfluoroalkyl-substituted,[6] (i) LDH-hosted and for 1-phenyl-1-cyclohexene over (j) MCM-41-supported,[32] (k) LDH-hosted and cyclohexene over (l) cationic salen-Mn(III)[35] and (m) LDH-hosted forms.

Very recently, Linker et al.[36] showed experimental evidence for radical pathways during the epoxidation of 1,4-cyclohexadienes using the Jacobsen's catalyst under homogeneous conditions. At this stage, the mechanism of the oxidation of alkenes over LDH-hosted Mn-salen catalyst is not known. Mechanistic studies as well as comparative studies with the use of the other transition metal-salen complexes into the LDH in the epoxidation of different alkenes as well as the use of other oxidants are in progress to help determine the role of the LDH host on the enantio- and diastereoselectivities.

The stability of the catalyst was studied by performing repeated epoxidation reactions using the same conditions as described above. At the end of each reaction cycle, the catalyst was recovered by filtration and washed with toluene, dried and reused. The results are shown in Tables 2 and 3 for catalyst reused up to three times. The conversion [%], selectivity [%] and ee [%] were almost identical irre-

spective of the number of cycles. No evidence for leaching of Mn or decomposition of the catalyst complex was observed during the catalysis reaction. No traces of Mn were detected in the liquid reaction mixture by AA spectroscopy. The FTIR spectrum of the solid catalyst after reuse was identical to the fresh catalyst.

Conclusions

LDH-[Mn(Cl)salen] was an excellent catalyst system for the asymmetric epoxidation of styrenes and cyclic alkenes. The LDH-[Mn(Cl)salen] gave good product selectivity and yield of the asymmetric epoxidation of styrenes and cyclic alkenes using molecular oxygen at atmospheric pressure with mild solvents. The fact that the LDH-hosted catalyst was active for these reactions under low molecular oxygen pressure (14.5 psi) using toluene as solvent is of significance in view of the current literature for asymmetric epoxidation catalysts for this reaction. The nature of the support environment is thought to play a significant role. The asymmetric induction was good, being higher or comparable with results obtained with salen-Mn(III) complex supported on zeolite or MCM-41 or using homogeneous perfluoroalkyl-substituted salen.[6,8,32]

The advantages of the present catalyst for the asymmetric epoxidation of styrenes and cyclic alkenes are:

1) The sulphonato-salen-manganese(III) complexes and hydrotalcite-based catalyst are readily prepared from aqueous medium without using organic solvents, unlike a large number of catalysts based on salen-metal complexes which are synthesised using chlorinated solvents.

2) Salt formation and the need to use low (below ambient) temperatures is avoided by the use of molecular oxygen/pivalaldehyde instead of NaOCl as used in Jacobsen's system.[5]

3) LDH-[Mn(Cl)salen] catalyst is highly active at room temperature in molecular oxygen as oxidant and toluene as solvent, instead of the chlorinated solvent used by others[8] to achieve maximum activity and selectivity.

Experimental Section

Preparation of Chiral Sulfonato-Salen Ligand, H_2L (1)

(*R,R*)-1,2-Diammoniumcyclohexane mono-(+)-tartrate[37] and sodium salicylaldehyde-5-sulfonate[38] were prepared using a literature method. A mixture of 2.97 g (11.2 mmol) of (*R,R*)-1,2-diammoniumcyclohexane mono-(+)-tartrate and 3.12 *g* (22.5 mmol) of potassium carbonate were combined with 20 mL of water-ethanol (1:4) into a two-necked round-bottomed flask with reflux condenser and an addition funnel. The mixture was heated and stirred with a magnetic stirrer. A solution of sodium salicylaldehyde-5-sulfonate (5.54 g, 22 mmol) in 20 mL of water was added dropwise to the above solution through an addition funnel with constant stirring and gentle heating (at 70 °C). The resulting mixture was heated at reflux for 1 h with stirring and cooled to room temperature. The volume was reduced by 50% by rotary-evaporation until a yellow solid separated, which was filtered off and washed with ethanol (200 mL). The yellow solid was then recrystallised from water-diethyl ether mixture and dried over silica gel; Yield: 98%.

Preparation of Na_2[Mn(Cl)salen]·2 H_2O (3)

To an aqueous solution (30 mL) of $Mn(O_2CMe)_2 \cdot 4\,H_2O$ (1.72 g, 7.0 mmol), an aqueous solution (20 mL) of the ligand **1** (1.75 g, 6.5 mmol) was added dropwise with stirring. Saturated aqueous sodium chloride solution (3 mL) was added to the mixture after the complete addition of ligand, stirring was continued for 1 h and the mixture allowed to stand for 2 h. The green solid was separated, filtered and washed with cold water (100 mL) and ethanol (100 mL) and dried over silica gel; yield: 97%.

Preparation of LDH-[Mn(Cl)salen] (4)

The LDH-[Mn(Cl)salen] was obtained by the partial substitution of intercalated C_6H_5COO ions by the $[Mn(Cl)salen]^{2-}$ ions. The LDH-[C_6H_5COO] was prepared by mixing a solution of zinc(II) nitrate tetrahydrate (29.75 g, 100 mmol), and aluminium(III) nitrate (12.50 g, 33.3 mmol) in de-carbonated water (100 mL), together with a further separate solution prepared by dissolving benzoic acid (21.96 g, 180 mmol) and NaOH (15.60 g, 390 mmol) in de-carbonated water (100 mL) under a nitrogen atmosphere. The gel-like mixture was digested at 348 K for 62 h. Upon cooling, the product was isolated by filtration, washed with water (700 mL) and ethanol (200 mL) and dried overnight at 333 K; yield: 90%.

Na_2[Mn(Cl)salen] (1.71 g, 2.51 mmol) was dissolved in de-carbonated water (50 mL) and LDH-[C_6H_5COO] (5.0 g) was added to the solution and stirred for 10 h at room temperature under a nitrogen atmosphere. The pale green product was filtered off and washed with water (300 mL) and dried at overnight at 333 K.

Catalytic Reaction

Catalytic epoxidation of styrenes and cyclic alkenes with molecular oxygen was carried out in a two-neck, round-bottom flask equipped with a condenser. In a typical run, 1 mmol of alkene, 2 mmol of pivalaldehyde, 10 mL of toluene and 0.050 g of catalyst were stirred at room temperature (298 K) while bubbling molecular oxygen at atmospheric pressure. Catalytic epoxidation of 1-methyl-1-cyclohexene with molecular oxygen at 100 psi was carried out in a stainless steel autoclave fitted with pressure sensor and stirrer and held at constant temperature using an external oil bath.

The reaction products and enantiomeric excess were determined using a Hewlett-Packard GC/MS fitted with CYDEX-B fused silica chiral column using both FID and MS detectors.

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[30] Data: For ligand (**1**): IR (KBr): ν(OH),3210;ν(CH=N), 1634; ν(C–O), 1522, ν(SO_3), 1110 and 1035 cm^{-1}; anal. found (%): C 45.72, H 3.79, N 5.36; calcd. (%) for $Na_2C_{20}H_{20}N_2S_2O_8$: C 45.61, H 3.84, N, 5.32. For ligand (**2**): IR:ν(C=N), 1623, ν(C–O), 1540, ν(SO_3), 1029 and 1117, ν(Mn–O), 573, ν(Mn–N), 430 cm^{-1}; UV-vis: λ = 798, 576, 466, 365, 295, 250; anal. found (%): C 38.93, H 3.76, N 4.10, Mn 8.23; calcd. (%) for $Na_2MnC_{22}H_{25}N_2S_2O_{12}$: C 39.17, H 3.74, N 4.15, Mn 8.15. For ligand (**3**): IR: ν(C=N), 1626, ν(C–O), 1545, ν(SO_3), 1026 and 1118, ν(Mn–O), 575, ν(Mn–N), 430 cm^{-1}; UV-vis (nujol mull): λ = 800, 574, 465, 363, 295, 250; anal. found: C 35.25, H 3.27, N 3.98, Mn 8.20; calcd. for $Na_2MnC_{20}H_{22}N_2S_2O_{12}Cl$: C 35.16, H 3.22, N 4.11, Mn 8.05. For LDH-[C_6H_5COO]: XRD: 2θ/° (d-spacing, Å): 5.8(15.22), 11.3(7.82), 17.0(5.21), 22.7(3.91); anal. found: Zn 34.61, Al 5.58, H_2O 8.83; calcd for LDH-[C_6H_5COO]: Zn 34.75, Al 5.67, H_2O 8.91. For **4**: XRD: 2θ/° (d-spacing,Å): 4.7(18.78), 8.6(10.27), 13.8(6.41), 19.7(4.50); anal. found (%): Zn 29.03, Al 4.69; [Mn(Cl)salen] 24.88, H_2O 7.53; calcd (%) for **4**: Zn 29.14, Al 4.81, [Mn(Cl)salen] 25.06, H_2O 7.47; UV-Vis (nujol mull): λ = 799, 552, 446, 350, 270, 226.

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