Epoxidation by layered double hydroxide-hosted catalysts. Catalyst synthesis and use in the epoxidation of R-(+)-limonene and (−)-α-pinene using molecular oxygen

Samiran Bhattacharjee and James A. Anderson*

Division of Physical and Inorganic Chemistry, University of Dundee, Dundee, DD1 4HN Scotland, UK

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A novel chiral sulphonato–salen–manganese(III) complex has been intercalated into a Zn(II)–Al(III) layered double hydroxide (LDH) host to produce a stable heterogeneous epoxidation catalyst. Powder X-ray diffraction, IR and UV–Visible (solid) spectroscopy and TGA confirmed the successful intercalation of the Mn complex within the LDH gallery height. The intercalated sulphonato–salen–manganese(III) complex was found to be an effective heterogeneous catalyst for the stereoselective epoxidation of R-(+)-limonene and (−)-α-pinene at room temperature and using molecular oxygen at atmospheric pressure as oxidant. At close to 100% conversion, R-(+)-limonene was converted into the corresponding epoxide with 93% selectivity and 43% de (diastereomeric excess), whereas (−)-α-pinene was converted with 93% selectivity and 98% de. The catalyst could be recycled without loss of efficiency.

KEY WORDS: chiral salen–manganese(III); layered double hydroxide; LDH host catalyst; R-(+)-limonene; (−)-α-pinene; epoxidation, heterogeneous catalysis.

1. Introduction

Much attention has recently been paid to the establishment of ecologically more acceptable catalytic processes, including removal of toxic reagents, minimization of by-product formation, low-cost and simple procedure. Epoxides are a useful synthetic intermediate in the manufacture of pharmaceuticals and some oxygenated monoterpenes are used in the flavors and perfumes industries.

Chiral porphyrin–metal complexes show high enantioselectivities for the epoxidation of terminal alkenes [1], although these modified porphyrins are difficult to synthesize. Schiff-base ligands derived from salicylaldehyde and chiral amines, known as ‘salen ligand’ and its manganese(III) complexes, developed by Jacobsen and co-workers [2] have been widely applied in enantioselective epoxidation reactions [3–8]. Despite high activity, selectivity and chiral induction, several disadvantages, such as deactivation, salt formation due to the use of sodium hypochlorite as oxidant and difficult separation of the catalyst after use, are inherent with this system. To overcome the latter problem, attempts to attach the active system to zeolites [4], to silica *via* chloropropyl spacers, metallated with manganese [5] and using organo-functionalized mesoporous materials [6] have been made and the anchored systems tested in the epoxidation of alkenes.

The use of clay minerals as catalysts or catalysts support has attracted much interest with much of this focused on the use of cationic clays [9]. Hydrotalcite-based materials have received attention in recent years as anion exchangers [10–12], as catalysts [13,14] and as catalyst precursors [15,16]. Studies on the intercalation of transition metal complexes within hydrotalcite layers are less abundant, although intercalation of a dioxomolybdenum(VI) anion into a Zn(II)–Al(III) layered double hydroxide (LDH) host is reported to show useful catalytic properties in the oxidation of thiols and reduction of nitrobenzene [17,18]. Recent advances in the pillaring of hydrotalcite by polyoxometalate anions have demonstrated that these materials may exhibit sufficiently large gallery heights to allow catalytic oxidation of larger organic compounds [19] including shape selective epoxidation of alkenes with H_2O_2 by changing the size of intercalating species [20]. LDH-OsO_4 catalysts have been shown to display good asymmetric dihydroxylation of olefins [14]. We recently reported [21] that chiral sulphonato–salen–manganese(III) complex intercalated into a Zn^{II}–Al^{III} LDH shows high conversion, selectivity and diasteriomeric excess (de) in the oxidation of R-(+)-limonene using 75–150 psi of molecular oxygen. While details of the catalytic activities with other alkenes using molecular oxygen and other oxidants are currently being pursued [22], the present paper deals with the synthesis of the LDH, $[Zn_{2.15}Al_{0.86}(OH)_{6.02}][Mn(Cl)(L)]_{0.19}[C_6H_5\ COO]_{0.48} \cdot 2H_2O$ as well as its action as a heterogeneous catalyst in the oxidation of R-(+)-limonene and (−)-α-pinene by molecular oxygen at atmospheric pressure. To our knowledge, intercalated

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*To whom correspondence should be addressed.
E-mail: j.a.anderson@dundee.ac.uk

systems containing chiral salen–manganese(III) complexes for the epoxidation of R-(+)-limonene and (−)-α-pinene using molecular oxygen at atmospheric pressure have not been previously reported.

2. Experimental methods

2.1. Preparation of metal complex catalyst

2.1.1. Preparation of sulphonato–salen–ligand, H_2L 3

(*R,R*)-1,2-diammoniumcyclohexane mono-(+)-tartatrate **1** [23] from *trans*-diaminocyclohexane (Aldrich) and (+)-tartaric acid (Aldrich), and sodium salicylaldehyde-5-sulphonate (**2**) [24] from salicylaldehyde (Aldrich) and aniline (Aldrich), were prepared using literature methods. A mixture of 2.97 g of (*R,R*)-1,2-diammoniumcyclohexane mono-(+)-tartatrate and 3.12 g of potassium carbonate were combined with 20 mL 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-sulphonate (5.54 g) in 20 mL of water was added dropwise to the above solution through an addition funnel with constant stirring and gentle heating. The resulting mixture was refluxed for 1 h with stirring and cooled to room temperature. The volume was reduced by 50% by rotary-evaporation until a yellow solid was separated, which was filtered off and washed with ethanol. The yellow solid was then recrystallized from water–diethyl ether mixture and dried over silica gel.

2.1.2. Preparation of $Na_2[Mn(OAc)(L)]\cdot 2H_2O$ 4

To an aqueous solution (30 mL) of $Mn(O_2CMe)_2 \cdot 4H_2O$ (1.72 g) (Aldrich) an aqueous solution (20 mL) of the ligand (1.75 g) was added dropwise with stirring. The stirring was continued for an hour and the mixture to remain left standing for 2 h. The green solid was separated and filtered and washed with cold water and ethanol and dried over silica gel.

2.1.3. Preparation of $Na_2[Mn(Cl)(L)] \cdot 2H_2O$ 5

Saturated aqueous sodium chloride (3 mL) was added to the mixture after the complete addition of ligand [as described for $Na_2[Mn(OAc)(L)] \cdot 2H_2O$] and stirring was continued for 1 h and the mixture allowed to stand for 2 h. The green solid was separated and filtered and washed with cold water and ethanol and dried over silica gel.

2.1.4. Preparation of LDH-[Mn(Cl)(L)] 6

The LDH-[Mn(Cl)(L)] obtained by the partial substitution of intercalated C_6H_5COO ions by the $[Mn(Cl)(L]^{2-}$ ions. The LDH-[C_6H_5COO] was prepared by mixing a solution of zinc(II) nitrate tetrahydrate (29.75 g) (Aldrich) and aluminium(III) nitrate (12.50 g) (Aldrich) in de-carbonated water, together with a further separate solution prepared by dissolving benzoic acid (21.96 g) and NaOH (15.60 g) in de-carbonated water 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 and ethanol and dried overnight at 333 K. $Na_2[Mn(Cl)(L)]$ (1.71 g) was dissolved in de-carbonated water 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 and dried at overnight 333 K.

2.1.5. Catalyst characterization

IR spectra of samples were recorded using KBr discs on a Perkin–Elmer 1720X FTIR spectrometer and electronic spectra on a Perkin–Elmer UV/VIS Spectrometer Lambda 16. The X-ray powder diffraction patterns were recorded on a Philips PW 1010 X-ray generator with CuK_α (1.5402 Å) radiation at 1^o min^{-1}. Thermogravimetric analysis, in the range 298–971 K, were carried out on a Mettler Toledo Star^e System under a flow of air and a heating rate of 5 K min^{-1}. Manganese and aluminium concentrations were estimated by literature methods [25] using UV–Visible and fluorescence spectroscopies, respectively, while zinc was determined using a UNICAM 939/959 atomic absorption spectrometer. Characterization details are given in tables 1 and 2.

2.2. Catalytic reaction

Catalytic epoxidation of R-(+)-limonene and (−)-α-pinene with molecular oxygen was carried out in a two-neck round bottom flask equipped with condenser. In a

Table 1
Characterization of catalyst precursors

Compound	Analytical data (%)[a]				λ_{max} (nm)[b]
	C	H	N	Mn	
H_2L **3**	45.72 (45.61)	3.74 (3.84)	5.36 (5.32)	–	–
$Na_2[Mn(OAc)(L)] \cdot 2H_2O$ **4**	38.93 (39.17)	3.76 (3.74)	4.10 (4.15)	8.23 (8.15)	800, 574, 465, 363, 295, 250
$Na_2[Mn(Cl)(L)] \cdot 2H_2O$ **5**	35.25 (35.16)	3.27 (3.22)	3.98 (4.11)	8.20 (8.05)	798, 576, 466, 365, 295, 250

[a] Calculated values are shown in parentheses.

[b] In Nujol mull.

Table 2
Characterization of the LDH-host precursor and hosted Mn(III) complex[a]

Compounds	Zn(%)	Al(%)	$[Mn(Cl)(L)]^2$ (%)	Λ_{max}[b]
LDH-$[C_6H_5COO]$	34.61 (34.75)	5.58 (5.67)	–	277, 234
LDH-[Mn(Cl)(L)] **6**	29.03 (29.14)	4.69 (4.81)	24.88 (25.06)	799, 552, 446, 350, 270, 226

[a] Calculated values are shown in parentheses.
[b] In Nujol mull.

typical run, 3.70 mmol of R-(+)-limonene, 9.2 mmol pivalaldehyde, 1.78 mmol *N*-methylimidazole and 0.100 g of catalyst **6** (containing 0.85% Mn) were stirred at room temperature (298 K) while bubbling molecular oxygen at atmospheric pressure. After 6 h the catalyst was filtered off and the selectivity and conversion measured using Perkin–Elmer GC Autosystem XL fitted with 10% SP 2330(100/120) Supelcoport capillary column. The reaction products were analysed using a Hewlett–packard GC/MS fitted with CYDEX-B fused silica chiral column.

3. Results and discussion

3.1. Synthesis of $[MnIII\text{-}(L)(X)]^{2-}$ and LDH-[Mn(Cl)(L)]

The chiral Schiff-base ligand **3** was prepared as a crystalline yellow solid (98% yield) by refluxing two equivalents of sodium salicylaldehyde-5-sulfonate **2** with (*R,R*)-1,2-diammoniumcylohexane mono-(+)-tartrate **1** in a water–ethanol medium. In aqueous solution, the chiral ligand instantly reacted with manganese(II) acetate tetrahydrate to produce dianionic manganese(III) **4** compound in ~95% yield and also to give $[Mn(Cl)(L)]^{2-}$ (**5**) with good yield (97%). $[Mn(Cl)(L)]^{2-}$ compound was intercalated into Zn(II)–Al(III) LDH at room temperature from aqueous medium by exchange of the benzoate ion. Although the aim was total elimination of the benzoate ion, only partial substitution by the manganese compound was achieved.

3.2. Characterization of $[MnIII\text{-}(L)(X)]^{2-}$ and LDH-[Mn(Cl)(L)] catalyst

The free Schiff-base ligand exhibits strong bands at 1108 and 1035 cm^{-1} in the IR spectrum (figure 1) due to the anti-symmetric and symmetric stretching modes of the SO_3^- moiety [26] and these are slightly blue-shifted in the Mn(III) complexes (figure 2). The NNOO (donors of ligand functionalities) mode of metal coordination, i.e., through the phenolic oxygen and azomethine nitrogen of the salen–ligand was apparent from the blue shift (ca. 23 cm^{-1}) of the ν(C–O) and the red shift (ca. 12 cm^{-1}) of the ν(C=N) vibrations of the free ligand (1522 and 1631 cm^{-1}, respectively) [27]. Further support for this coordination mode is provided by bands at ca. 574 and 425 cm^{-1} due to the ν(Mn—O) and ν(Mn–N), respectively [27]. The IR spectrum (figure 2) of catalyst **6** shows bands at 1116 and 1032 cm^{-1} due to the presence of the sulphonato group and at 573 cm^{-1} for ν(Mn–O), indicating the presence of the $[Mn(Cl)(L)]^{2-}$ ion within the LDH. Bands in the region 1650–1500 cm^{-1} (figure 2) are not readily assignable due to the co-existence of carboxylato and phenyl ring vibration in LDH-$[C_6H_5COO]$. A broad band around 3430 cm^{-1} in the

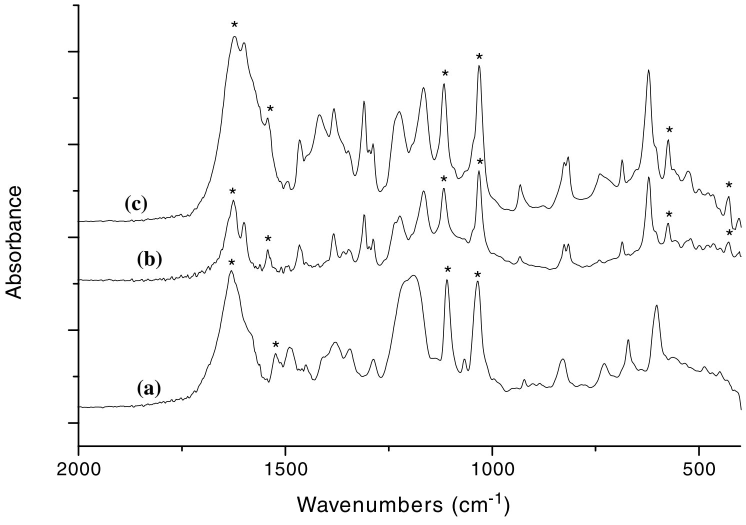


Figure 1. IR spectra of (a) free sulphonato–salen, (b) $Na_2[Mn(Cl)(L)]$ and (c) $Na_2[Mn(OAc)(L)]$.

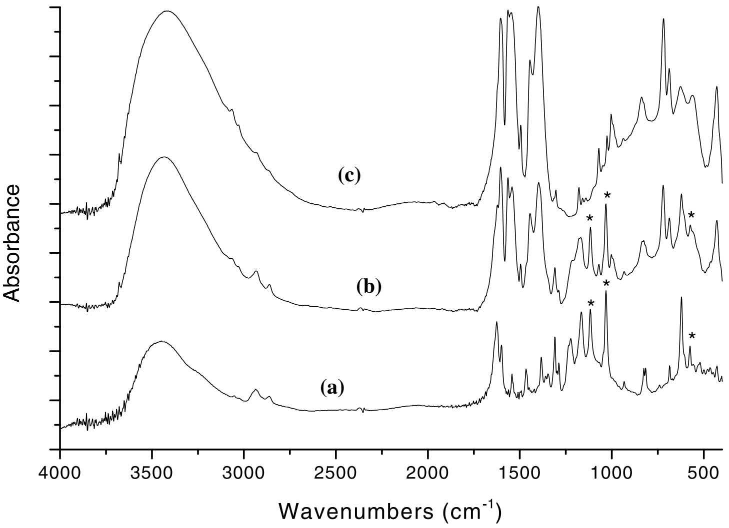


Figure 2. IR spectra of (a) $Na_2[Mn(Cl)(L)]$, (b) LDH-[Mn(Cl)(L)] and (c) LDH-[C_6H_5COO].

spectra of both LDH-[C_6H_5COO] and LDH-[Mn(L)(Cl)] is attributed to the stretching mode of hydrogen bonded hydroxyl groups and water molecules.

The X-ray powder diffraction patterns of LDH-[C_6H_5COO] and LDH-[Mn(Cl)(L)] showed that the basal spacing of the LDH-[C_6H_5COO] was increased from 15.22 to 18.78 Å following the exchange process. The gallery height of the catalyst is 14.1 Å when the thickness of the brucite layers (4.7 Å) was subtracted. This increase in the gallery height strongly suggests the intercalation of the $[Mn(L)(Cl)]^{2-}$ ion. The calculated dimension of chloro[*N*,*N*′-bis(salicylidene)-cyclohexanediamine]-manganese(III) is 13.0 Å [28]. Elemental analysis (table 2) for the catalyst is consistent with the formula unit $[Zn_{2.15}Al_{0.86}(OH)_{6.02}][Mn(Cl))L)]_{0.19}[C_6H_5COO]_{0.48} \cdot 2\,H_2O$. The ratio [Al/(Zn + Al)] of catalyst **6** and LDH-[C_6H_5COO] are almost identical, indicating that no loss of either Zn^{II} or Al^{III} occurred during the exchange procedure.

The thermo-gravimetric analysis curves of LDH-[Mn(L)(Cl)], LDH-[C_6H_5COO] and the free manganese(III) complex are shown in figure 3. The mass loss behaviour of the latter showed decomposition of the complex occurred between 515 and 583 K. A similar mass loss was found for catalyst **6**, but no weight loss was observed for the LDH-[C_6H_5COO] between 503 and 583 K. This mass loss results from decomposition of the manganese complex and is consistent with the presence of the Mn(III) complex **5** within the LDH host.

The electronic spectra of the free manganese(III) complex **4** (in Nujol mull) displayed bands at 800, 574, 465, 363, 295 and 250 nm (table 1). Of these, bands at 800 and 574 nm are due to $^5B_1 \rightarrow {}^5B_2$, and $^5B_1 \rightarrow {}^5A_1$ transitions [27,29]. The UV–Visible spectrum (table 2) of catalyst **6** (in Nujol mull) showed similar features to the free complex, indicating that following intercalation, no change to the manganese(III) co-ordination centre took place.

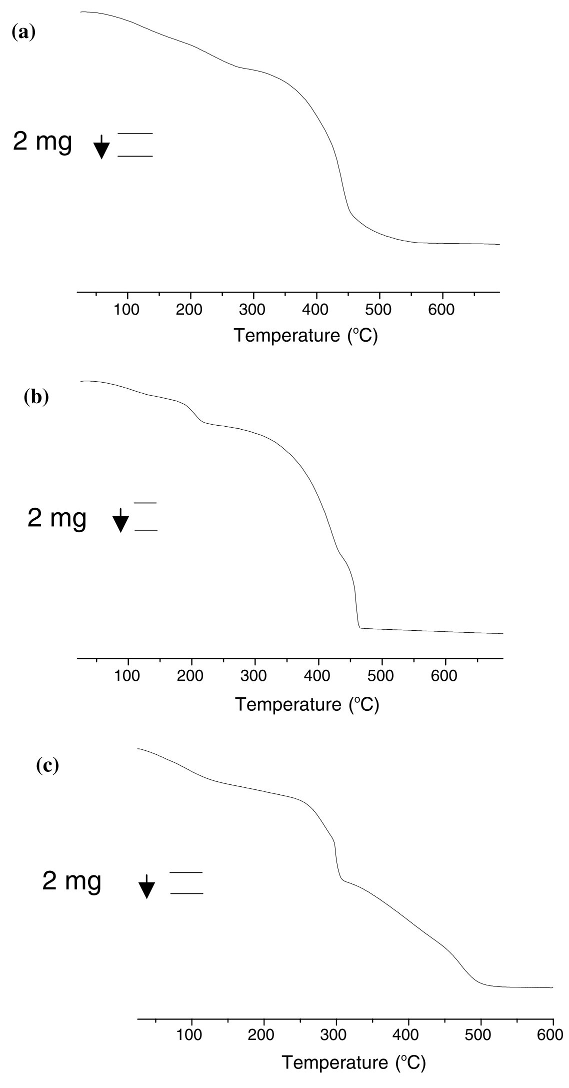
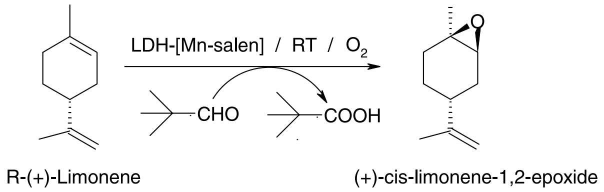


Figure 3. TGA curves of (a) LDH-[Mn(Cl)(L)], (b) LDH-[C_6H_5COO] and (c) free chiral sulphonato–manganese(III) complex **5** in air.

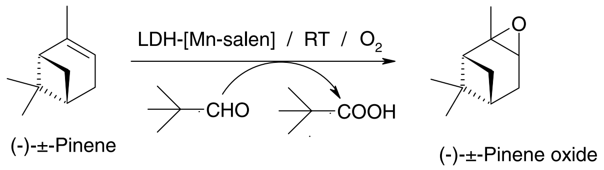
On the basis of the XRD data, a possible configuration for the Mn complex **5** within the interlayer spacing is shown in figure 4.

3.3. Catalytic activity of the oxidation of alkenes

The LDH-[Mn(Cl)(L)] catalyst was tested in the epoxidation of R-(+)-limonene and (−)-α-pinene using molecular oxygen at atmospheric pressure (14.5 psi) and at 298 K. A combination of pivalaldehyde and catalytic amounts of *N*-methyimidazole was used, under identical reaction conditions as those reported by Mukaiyama and co-workers [30]. The reactions are expressed by equations (1) and (2).



(1)



(2)

The epoxidation of R-(+)-limonene was tested at atmospheric pressure using toluene as solvent. The results are summarised in tables 3–4. Using pivalaldehyde at 298 K, R-(+)-limonene was converted into (+)-*cis*-limonene-1,2-epoxide with 88.5% selectivity and 33.4% de (table 3). The other detected products were the corresponding diepoxide and diol, both resulting from secondary reactions. Addition of catalytic amounts of *N*-methylimidazole, improved the de to 42.8% while the selectivity was increased to 93.3%. Similar observations [30] were found in the epoxidation of 1,2-dihydronaphthalenes, where the epoxide ee% was increased by using *N*-methylimidazole. The comparative data displayed in figure 5 shows that epoxidation of R-(+)-limonene using the present LDH based catalyst gave much higher selectivity than those previously reported for zeolite entrapped Mn–salen [31], whereas, the de was similar for both systems.

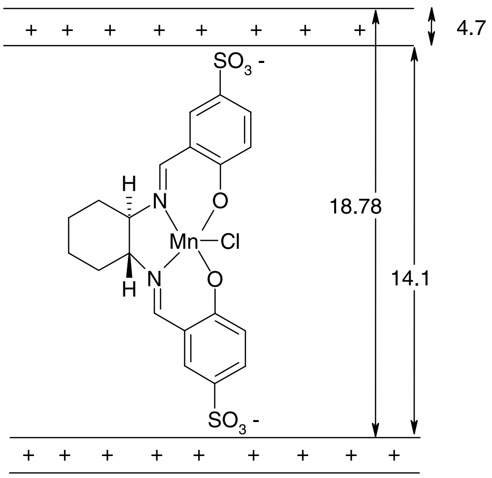


Figure 4. Postulated configuration of the intercalated ion **5** in the interlayer space of the LDH.

Table 3
Epoxidation of R-(+)-limonene and (−)-α-pinene[a]

Substrate	Additive	Conversion(%)	Selectivity(%)	de(%)
R-(+)-limonene	–	96.6	88.5	33.4
R-(+)-limonene	*N*-MeI[b]	94.7	93.3	42.8
(−)-α-pinene	–	100.0	90.0	98.1
(−)-α-pinene	*N*-MeI[b]	100.0	93.3	98.3

[a] Reaction conditions: 3.7 mmol substrate, 9.2 mmol pivalaldehyde, 18.5 mL toluene, 0.100 g catalyst, 14.5 psi molecular oxygen, temperature 298 K and 6 h.

[b] *N*-methylimidazole, 1.78 mmol.

Table 4
Performance of reused catalyst in the epoxidation of (−)-α-pinene[a]

Run	Conversion(%)	Selectivity(%)	de(%)
1	100	90.0	98.1
2	100	93.3	98.1
3	100	89.7	98.1

[a] Reaction condition: 3.7 mmol (−)-α-pinene, 9.2 mmol pivalaldehyde, 18.5 mL toluene, 0.100 g catalyst and molecular oxygen (14.5 psi), temperature 298 K and 6 h.

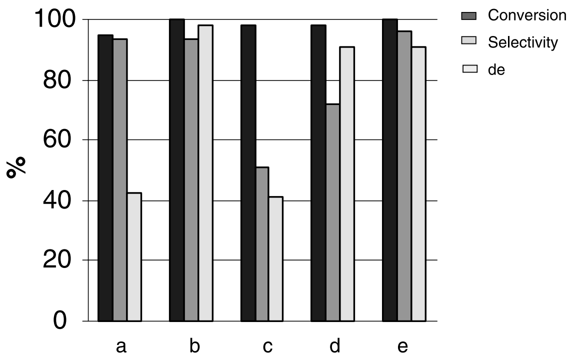


Figure 5. Comparison of conversion, selectivity and de (%) of R-(+)-limonene over (a) LDH hosted Mn–salen complex and (c) zeolite immobilized Mn(salen-2) [31], and for (−)-α-pinene over (b) LDH hosted Mn–salen complex, (d) zeolite immobilized Mn(salen-2) [31] and (e) zeolite immobilized Co(salen) [31].

The epoxidation of (−)-α-pinene at 298 K was also investigated. Under atmospheric pressure of O_2, (−)-α-pinene was converted to (−)-α-pinene oxide with high conversion, selectivity and de (table 3). In this case, selectivity and de were not affected by the presence of the donor ligand, *N*-methylimidazole. Using atmospheric pressure of oxidant, the conversion, selectivity and de were higher than those reported for zeolite entrapped Mn–salen Jacobsen's catalyst [31]. An immobilized cobalt–salen complex [31] was found to produce the highest catalytic activity in a series of zeolite entrapped metal–salen systems. A comparison of data obtained for (–)-α-pinene epoxidation is shown in figure 5. The modified Jacobsen's catalyst shows higher conversion, selectivity and de, in the presence of the LDH catalyst than zeolite entrapped Mn–salen [31] either in homogeneous or heterogeneous systems. A higher de but slightly lower selectivity was also found for our catalyst when compared with recently reported results for zeolite entrapped Co–salen catalyst [31]. The present results are at odds with the claim [31] that Jacobsen's catalyst is not particularly suited for the (–)-α-pinene epoxidation reaction indicating that the use of the LDH as host provides some additional features to the catalytic process.

The above results suggest that the epoxidation of R-(+)-limonene and (–)-α-pinene within the LDH does not proceed in an identical manner to the reaction when performed using zeolite entrapped catalysts. The present results suggest that de and selectivity are not only dependent on the ligand substituents or the central metal ion, but possibly also on the presence of positive charge interaction of the layered hydroxides host and the gallery height. The origin of the high catalytic activity may also be associated with a sufficiently large gallery spacing of the LDH-[Mn(Cl)(L)] catalyst which allowed greater accessibility of the substrate to interact with the active centre of the Mn(III)–salen complex between the double hydroxide layers.

The stability of the catalyst was studied by performing repeated epoxidation reactions using the same reaction 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 table 4 for catalyst reused up to three times. The conversion(%), selectivity(%) and de(%) were almost identical irrespective of the number of cycles. No evidence for leaching of Mn or decomposition of the catalyst complex was observed during the catalysis reaction and no Mn could be detected by AA spectroscopic measurement of the liquid reaction mixture after catalytic reaction. The IR spectrum of the solid catalyst after reuse was also identical to the fresh catalyst.

The advantages of the present catalyst for epoxidation reactions are:

(1) Salt formation is avoided by the use of molecular oxygen instead of sodium hypochloride as oxidant as used in Jacobsen's system [2]
(2) LDH-[Mn(Cl)(L)] catalyst is highly active at room temperature using toluene as solvent, instead of the more corrosive fluorobenzene used by others [31] to achieve maximum conversion%, de% and selectivity%.
(3) The use of oxygen at atmospheric pressures overcomes the need for complex pressure vessels which are inherent to a system using elevated oxygen pressures.

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 olefins as well as the use of other oxidants are in progress to understand the role of the LDH host on the enantio- and diastereoselectivities.

4. Conclusions

The chiral SO_3^-salen–Mn(III) complex intercalated into Zn/Al-LDH has been prepared and tested for its epoxidation activity using R-(+)-limonene and (–)-α-pinene as model compounds using molecular oxygen as oxidant at atmospheric pressure and at 298 K. The chiral salen ligand and metal complexes synthesized in this study from aqueous medium were obtained in high yield and high purity. In the case of R-(+)-limonene and (–)-α-pinene epoxidation, the LDH-[Mn(Cl)(L)] catalyst showed higher conversion, selectivity and de% compared with other published data for other Mn–salen catalysts.

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