

# Synthesis and application of layered double hydroxide-hosted catalysts for stereoselective epoxidation using molecular oxygen or air

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## Abstract

A novel chiral sulfonato-salen manganese(III) complex has been intercalated into a Zn(II)–Al(III) layered double hydroxide (LDH) host to produce a stable, active, and selective heterogeneous epoxidation catalyst. Powder X-ray diffraction, TGA, and IR and UV–visible spectroscopies confirm the successful intercalation of the Mn complex within the LDH structure. Molecular modeling calculations predict the orientation of the complex within the layered structure. The intercalated sulfonato-salen–manganese(III) complex was found to be effective in the stereoselective epoxidation of *R*-(+)-limonene and (–)- $\alpha$ -pinene at room temperature. At close to 100% conversion, *R*-(+)-limonene was converted to the corresponding epoxide with good selectivity and de (diastereomeric excess), whereas (–)- $\alpha$ -pinene was converted with 91.7% selectivity and 98.1% de. A significant advantage of this catalyst over the equivalent homogeneous counterpart was the ability to activate oxygen or air at atmospheric pressures in place of NaOCl. The catalyst could be recycled without loss of efficiency.

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**Keywords:** Chiral salen–manganese(III); Layered double hydroxide; LDH host catalyst; *R*-(+)-Limonene; (–)- $\alpha$ -Pinene; Heterogeneous air epoxidation

## 1. Introduction

Much attention has been paid over recent years to the establishment of ecologically acceptable processes in the chemicals industries. Approaches involve reducing the extent of by-product formation by using heterogeneous catalysts in place of stoichiometric reagents and employing reagents which maximise atom efficiency. One example of the former would be the use of solid acid catalysts to replace corrosive, liquid mineral acids for reactions such as isomerisation and alkylation. Maximising atom efficiency in, for example, an oxidation reaction might be achieved by the use of oxygen or air as an oxidising agent instead of the use of NaOCl, H<sub>2</sub>O<sub>2</sub> or peroxy acids.

One important oxidation reaction employed in industry as a route to the formation of useful intermediates is epoxidation. Additionally, some oxygenated monoterpenes are currently used in the flavors and perfumes industries. In recent years, much attention has been given to the development of routes for the preparation of enantiomerically

pure epoxides [1]. Among these, epoxidation of the appropriate alkene catalyzed under homogeneous conditions by chiral salen–Mn(III) complexes are an efficient synthesis method [2]. Collman et al. [3] showed that cytochrome P450 analogs (manganese porphyrin complexes) catalyzed the epoxidation of olefins while chiral iron–porphyrin complexes show high enantioselectivities in the epoxidation of terminal alkenes [4]. Unfortunately, these modified porphyrins are rather difficult to synthesize. Jacobsen et al. [5] reported catalytically active compounds prepared from more readily synthesized Mn(III) salen complexes that gave high enantioselectivities for the epoxidation of unfunctionalized alkenes under homogeneous conditions and using sodium hypochlorite as oxidant. Despite high activity, selectivity, and chiral induction, this system has several disadvantages including the use of sodium hypochlorite and the difficulty in recovering the catalyst after use. In an attempt to overcome the problem of catalyst recovery, one approach has been to attach the active system to zeolites [6], to silica via chloropropyl spacers, metallated with manganese [7] or using organo-functionalized mesoporous materials [8]. These anchored systems have shown reasonable properties in the epoxidation of alkenes. Kureshy et al. [9] recently reported

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immobilization of dicationic chiral Mn (III) complexes between the layers of a montmorillonite clay. This system was tested in the epoxidation of nonfunctionalized alkenes using NaOCl as oxidant and gave a higher ee for certain alkenes compared to that found under homogeneous conditions.

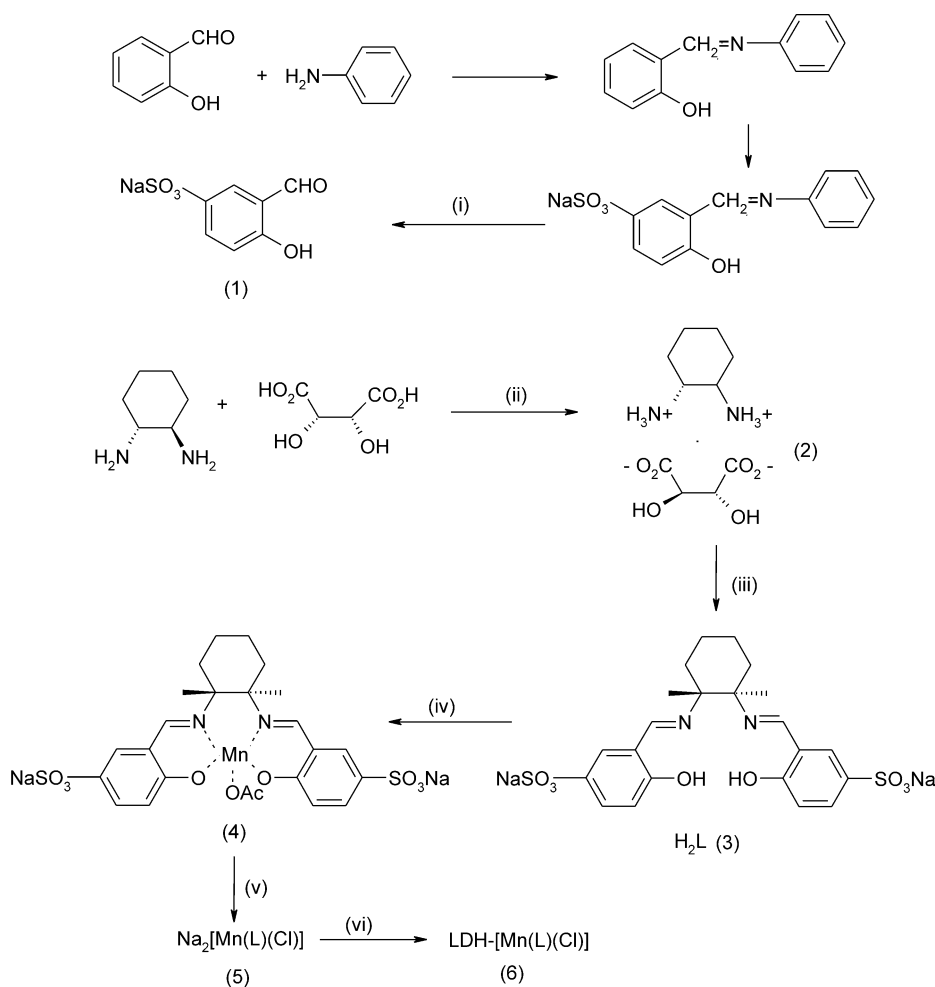
Among the different layered structures which might be considered as potential hosts, hydrotalcite-based materials have received attention over recent years in applications such as anion exchangers and catalysts [10–16]. Studies on the intercalation of transition-metal complexes within hydrotalcite layers are less abundant, although intercalation of a dioxomolybdenum(VI) anion into a Zn(II)–Al(III) layered double hydroxide host was reported to show useful catalytic properties in the oxidation of thiols [17] and reduction of nitrobenzene [18]. Recent advances in the pillaring of hydrotalcites by polyoxometalate anions have demonstrated that the gallery height may be increased sufficiently to allow oxidation of larger dimension organic compounds [19,20]. We have recently reported [21] that chiral sulfonato-salen–manganese(III) complex intercalated into a Zn<sup>II</sup>–Al<sup>III</sup> layered double hydroxide showed high conversion, selectivity, and de in the oxidation of (*R*)-limonene using elevated pres-

sure 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 and characterisation of the LDH, [Zn<sub>2.15</sub>Al<sub>0.86</sub>(OH)<sub>6.02</sub>][Mn(Cl)(L)]<sub>0.19</sub>[C<sub>6</sub>H<sub>5</sub>COO]<sub>0.48</sub> · 2H<sub>2</sub>O as well as its action as a heterogeneous catalyst in the epoxidation of (*R*)-limonene and (–)- $\alpha$ -pinene by molecular oxygen as well as in air at atmospheric pressure and using a range of benign solvents. To our knowledge, this represents the first report of the successful use of a heterogenised system containing a chiral salen–manganese(III) complex for the epoxidation of (*R*)-limonene and (–)- $\alpha$ -pinene at room temperature using air at atmospheric pressure.

## 2. Experimental methods

### 2.1. Preparation of metal complex catalyst

A scheme of the preparation procedure is shown in Scheme 1.



Scheme 1. (i) Ref. [24]; (ii) Ref. [23]; (iii) 5.54 g of **1** and 2.97 g of **2**; (iv) 1.72 g Mn(O<sub>2</sub>CMe)<sub>2</sub> · 4H<sub>2</sub>O and 1.75 g of **3**, water; (v) saturated NaCl solution; (vi) 5.0 g LDH-[C<sub>6</sub>H<sub>5</sub>COO] and 1.71 g of **5**, water, and stirred.

### 2.1.1. Preparation of sulfonato-salen ligand, H<sub>2</sub>L (3)

(*R,R*)-1,2-Diammoniumcyclohexane mono-(+)-tartrate (2) from *trans*-diaminocyclohexane (99%, Aldrich) and (*2R,3R*)-(+)-tartaric acid (99.5%, Aldrich) and sodium salicylaldehyde-5-sulfonate (1) from salicylaldehyde (98%, Aldrich) and aniline (99.5%, Aldrich) were prepared using published methods [23,24]. A mixture of 2.97 g of (*R,R*)-1,2-diammonium cyclohexane mono-(+)-tartrate 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-sulfonate (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 recrystallised from water–diethyl ether mixture and dried over silica gel. Yield: 98%.

### 2.1.2. Preparation of Na<sub>2</sub>[Mn(OAc)(L)] · 2H<sub>2</sub>O (4)

To an aqueous solution (30 ml) of Mn(O<sub>2</sub>CMe)<sub>2</sub> · 4H<sub>2</sub>O (1.72 g) (99+%, Aldrich), an aqueous solution (20 ml) of the ligand (1.75 g) was added dropwise while stirring. Stirring was continued for 1 h and the mixture left standing for 2 h. The green solid was separated and filtered and washed with cold water and ethanol and dried over silica gel. Yield: 95%.

### 2.1.3. Preparation of Na<sub>2</sub>[Mn(Cl)(L)] · 2H<sub>2</sub>O (5)

A saturated aqueous solution of sodium chloride (3 ml) was added to the mixture after the complete addition of ligand [as describe for Na<sub>2</sub>[Mn(OAc)(L)] · 2H<sub>2</sub>O] 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. Yield: 97%.

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

The LDH-[Mn(Cl)(L)] was obtained by the partial substitution of intercalated C<sub>6</sub>H<sub>5</sub>COO ions by the [Mn(Cl)(L)]<sup>2-</sup> ions. The LDH-[C<sub>6</sub>H<sub>5</sub>COO] was prepared by mixing a solution of zinc(II) nitrate tetrahydrate (29.75 g) (98%, Aldrich) and aluminum(III) nitrate (12.50 g) (99.997%, Aldrich) in decarbonated water, together with a further separate solution prepared by dissolving benzoic acid (21.96 g) and NaOH (15.60 g) in decarbonated 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. Yield: 90%.

Na<sub>2</sub>[Mn(Cl)(L)] (1.71 g) was dissolved in decarbonated water and LDH-[C<sub>6</sub>H<sub>5</sub>COO] (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. Yield: 90%.

### 2.1.5. Catalyst characterisation

IR spectra of samples were recorded using KBr disks 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 Cu-K<sub>α</sub> (1.5402 Å) radiation at 1° min<sup>-1</sup>. Thermogravimetric analyses, in the range 298–971 K, were carried out on a Mettler Toledo Star<sup>e</sup> System under a flow of air and a heating rate of 5 K min<sup>-1</sup>. Manganese and aluminum concentrations were estimated by literature methods [25] using UV–vis and fluorescence spectroscopies, respectively, while zinc was determined using a UNICAM 939/959 atomic absorption spectrometer. Characterisation details are given in Table 1.

### 2.2. Catalytic reaction

Epoxidation of (*R*)-limonene and (–)- $\alpha$ -pinene over the LDH-[Mn(L)(Cl)] catalyst with molecular oxygen or air was carried out in a twin-necked round-bottom flask equipped with condenser. In a typical run, 3.70 mmol of (*R*)-limonene,

Table 1  
Characterisation of catalyst precursors, the LDH-host precursor, and hosted Mn(III) complex

Compound	Analytical data <sup>a</sup> (%)						[Mn(Cl)(L)] <sub>2</sub> (%)	$\lambda_{\max}^b$ (nm)
	C	H	N	Mn	Zn	Al		
H <sub>2</sub> L (3)	45.72 (45.61)	3.74 (3.84)	5.36 (5.32)	–	–	–	–	–
Na <sub>2</sub> [Mn(OAc)(L)] · 2H <sub>2</sub> O (4)	38.93 (39.17)	3.76 (3.74)	4.10 (4.15)	8.23 (8.15)	–	–	–	800, 574, 465, 363, 295, 250
Na <sub>2</sub> [Mn(Cl)(L)] · 2H <sub>2</sub> O (5)	35.25 (35.16)	3.27 (3.22)	3.98 (4.11)	8.20 (8.05)	–	–	–	798, 576, 466, 365, 295, 250
LDH-[C <sub>6</sub> H <sub>5</sub> COO]					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

<sup>a</sup> Calculated values are shown in parentheses.

<sup>b</sup> In Nujol mull.

9.2 mmol pivalaldehyde, 1.78 mmol *N*-methylimidazole, and 0.100 g of catalyst (0.85% Mn) were stirred at room temperature (298 K) while bubbling molecular oxygen or air at atmospheric pressure. After completion of the reaction, the catalyst was filtered off and the selectivity and conversion were measured using a Perkin-Elmer GC Autosystem XL fitted with 10% SP 2330(100/120) Supelcoport capillary column and a FID. The reaction products were analysed using a Hewlett Packard GC/MS (with FID also) after separation over a CYDEX-B fused silica chiral column.

### 2.3. Computational details

The structure of the chiral (sulfonato-salen)-manganese(III) complex was calculated using the Gaussian 98 program [26], with the hybrid SCF-DFT method B3-LYP. This incorporates Becke's three-parameter Hybrid Functional [27] and the Lee, Yang, and Parr correlation functional [28], and generally gives superior results to HF-SCF calculations, which neglect the effects of electron correlation. There is no published crystal structure of this complex for comparison, so the structure of a related complex, chloro-(1*R*,2*R*)-(–)-(1,2-cyclohexanediamino-*N,N'*-bis(3,5-di-*t*-butyl-salicylidene))-manganese(III) [29] was used to provide an initial estimate of the geometry prior to optimisation. Geometry optimisation was performed with the LanL2DZ basis set, which employs Dunning–Huzinaga double zeta (DZ) basis functions [30] on C, H, N, and O and Los Alamos effective core potential with DZ functions on Mn, Cl, and S [31]. This effective core potential basis set was judged to be a reasonable compromise in view of the large size of the complex.

## 3. Results and discussion

### 3.1. Synthetic aspect of $[Mn^{III}-(\text{sulfonato-salen})(X)]^{2-}$

The synthetic route of chiral (sulfonato-salen)-manganese(III) and its LDH compound is shown in Scheme 1. The chiral Schiff base ligand (**3**) was readily prepared as a beautiful crystalline yellow solid in 98% yield by refluxing two equivalents of sodium salicylaldehyde-5-sulfonate (**1**) with (*R,R*)-1,2-diammoniumcyclohexane mono-(+)-tartrate (**2**) 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. The acetyl ligand in  $[Mn(OAc)(L)]^{2-}$  [ $L^{2-}$  = chiral salen (sulfonato)] was readily replaced by chloride at room temperature to give  $[Mn(Cl)(L)]^{2-}$  (**5**) with good yield (97%). The manganese compounds are water soluble.

### 3.2. Synthesis of LDH-[Mn–Salen]

The host hydrocalcite-like material,  $ZnAl-[C_6H_5COO]$  was prepared (see experimental section for details) by copre-

cipitation of a solution of zinc and aluminum nitrates with an aqueous solution of NaOH and benzoic acid.  $[Mn(Cl)(L)]^{2-}$  compound was intercalated into the zinc(II)–aluminum(III) layered double hydroxide at room temperature from aqueous medium by the exchange of the benzoate ion. Although complete elimination of the benzoate ion was the objective, only partial substitution by the manganese compound was achieved.

### 3.3. Characterisation of $[Mn^{III}-(L)(X)]^{2-}$ and LDH-[Mn(Cl)(L)] catalysts

The free Schiff-base ligand exhibits strong bands at 1110 and 1035  $cm^{-1}$  in the IR spectrum (Fig. 1A) due to the antisymmetric and symmetric stretching modes of the  $SO_3^-$  moiety [32] and these are slightly blue-shifted in the Mn(III)

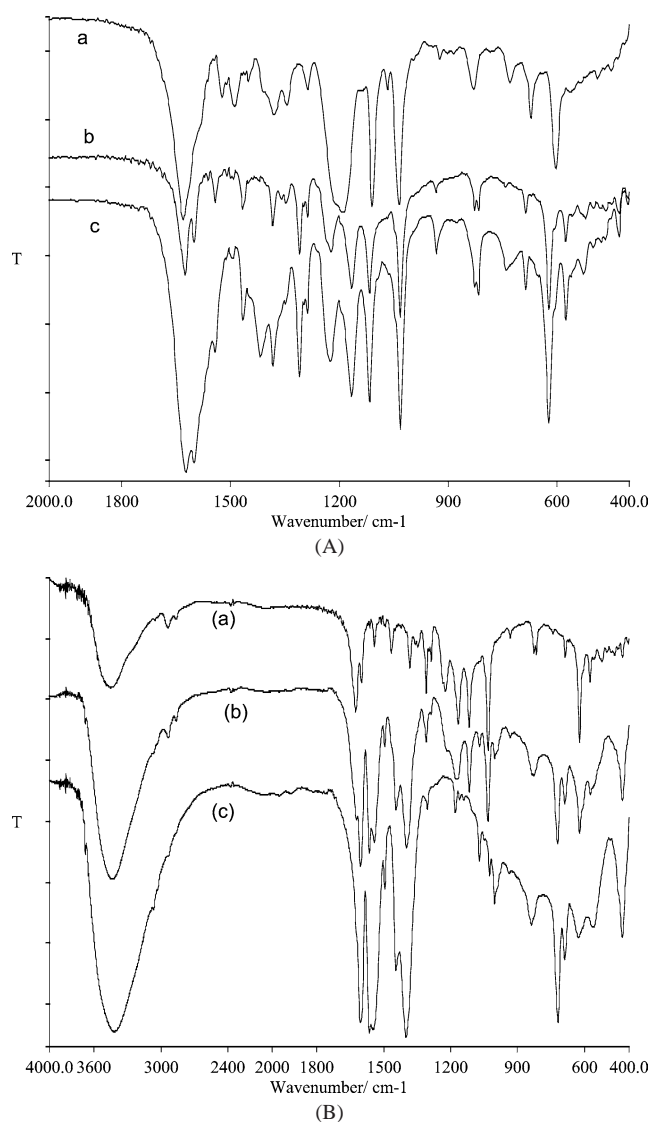


Fig. 1. (A) IR spectra of (a) free sulfonato-salen, (b)  $Na_2[Mn(Cl)(L)]$ , and (c)  $Na_2[Mn(OAc)(L)]$  and (B) (a)  $Na_2[Mn(Cl)(L)]$ , (b) LDH-[Mn(Cl)(L)], and (c) LDH-[ $C_6H_5COO$ ].

complexes (Fig. 1A). 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.  $23\text{ cm}^{-1}$ ) of the  $\nu(\text{C}-\text{O})$  and the red shift (ca.  $12\text{ cm}^{-1}$ ) of the  $\nu(\text{C}=\text{N})$  vibrations of the free ligand ( $1522$  and  $1632\text{ cm}^{-1}$  respectively) [33]. Further support for this coordination mode is provided by bands at ca.  $574$  and ca.  $425\text{ cm}^{-1}$  due to the  $\nu(\text{Mn}-\text{O})$  and  $\nu(\text{Mn}-\text{N})$ , respectively [33]. The IR spectrum (Fig. 1B) of catalyst **6** shows bands at  $1116$  and  $1032\text{ cm}^{-1}$  due to the presence of the sulfonato group and at  $573\text{ cm}^{-1}$  for  $\nu(\text{Mn}-\text{O})$ , indicating the presence of the  $[\text{Mn}(\text{Cl})(\text{L})]^{2-}$  ion within the layered double hydroxide. Bands in the region  $1650$ – $1500\text{ cm}^{-1}$  (Fig. 1B) are not readily assignable due to the coexistence of carboxylato and phenyl ring vibration in  $\text{LDH}[\text{C}_6\text{H}_5\text{COO}]$ . A broad band around  $3430\text{ cm}^{-1}$  in the spectra of both  $\text{LDH}[\text{C}_6\text{H}_5\text{COO}]$  and  $\text{LDH}[\text{Mn}(\text{L})(\text{Cl})]$  is attributed to the stretching mode of hydrogen-bonded hydroxyl groups and water molecules.

The X-ray powder diffraction patterns (Fig. 2) of  $\text{LDH}[\text{C}_6\text{H}_5\text{COO}]$  and  $\text{LDH}[\text{Mn}(\text{Cl})(\text{L})]$  showed that the basal spacing of the  $\text{LDH}[\text{C}_6\text{H}_5\text{COO}]$  was increased from  $15.22$  to  $18.78\text{ \AA}$  following the exchange process. The gallery height of the catalyst is  $14.1\text{ \AA}$  when the thickness of the brucite layers ( $4.7\text{ \AA}$ ) was subtracted. This increase

in the gallery height may be indicative of the intercalation of the  $[\text{Mn}(\text{L})(\text{Cl})]^{2-}$  ion. The calculated dimension of chloro[*N,N'*-bis(salicylidene)-cyclohexanediamine]-manganese-(III) is  $13.0\text{ \AA}$  [35]. Elemental analysis (Table 1) for the catalyst is consistent with the formula unit  $[\text{Zn}_{2.15}\text{Al}_{0.86}(\text{OH})_{6.02}][\text{Mn}(\text{Cl})(\text{L})]_{0.19}[\text{C}_6\text{H}_5\text{COO}]_{0.48} \cdot 2\text{H}_2\text{O}$ . The ratios  $[\text{Al}/(\text{Zn} + \text{Al})]$  of catalyst **6** and  $\text{LDH}[\text{C}_6\text{H}_5\text{COO}]$  are almost identical, indicating that no loss of either  $\text{Zn}^{\text{II}}$  or  $\text{Al}^{\text{III}}$  occurred during the exchange procedure.

The thermogravimetric analysis and first derivatives curves of  $\text{LDH}[\text{Mn}(\text{L})(\text{Cl})]$ ,  $\text{LDH}[\text{C}_6\text{H}_5\text{COO}]$ , and the free manganese(III) complex are shown in Fig. 3. The mass loss behaviour of the latter showed that decomposition of the complex occurred between  $515$  and  $583\text{ K}$  (Fig. 3A). A similar mass loss was found for catalyst **6** (Fig. 3C), but no weight loss was observed for the  $\text{LDH}[\text{C}_6\text{H}_5\text{COO}]$  between  $503$  and  $583\text{ K}$  (Fig. 3B). 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 field-free  $^5\text{D}$  term of manganese (III) in weak  $\text{O}_h$  field is split into a  $^5\text{E}_g$  ground and a  $^2\text{T}_g$  excited state. Since the ground state is an orbital doublet, Jahn–Teller distortion becomes pronounced giving rise to a five-coordinate square pyramidal situation. To a reasonable approximation,

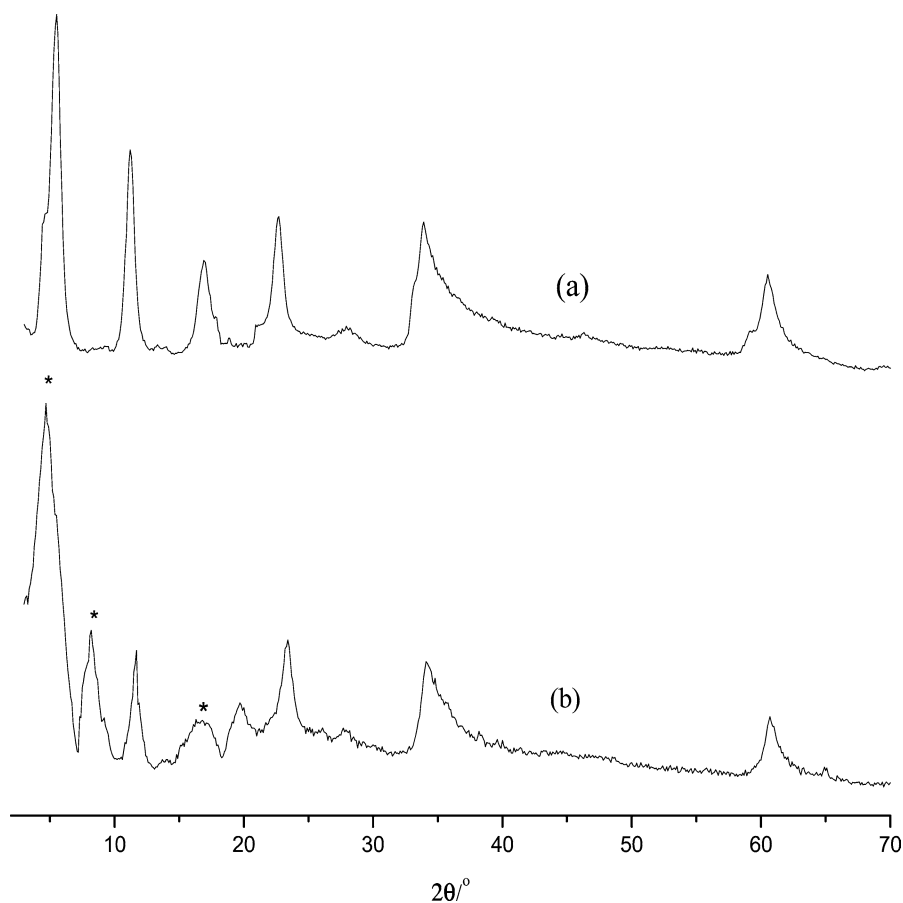


Fig. 2. X-ray powder patterns of (a)  $\text{LDH}[\text{C}_6\text{H}_5\text{COO}]$  and (b)  $\text{LDH}[\text{Mn}(\text{Cl})(\text{L})]$ .

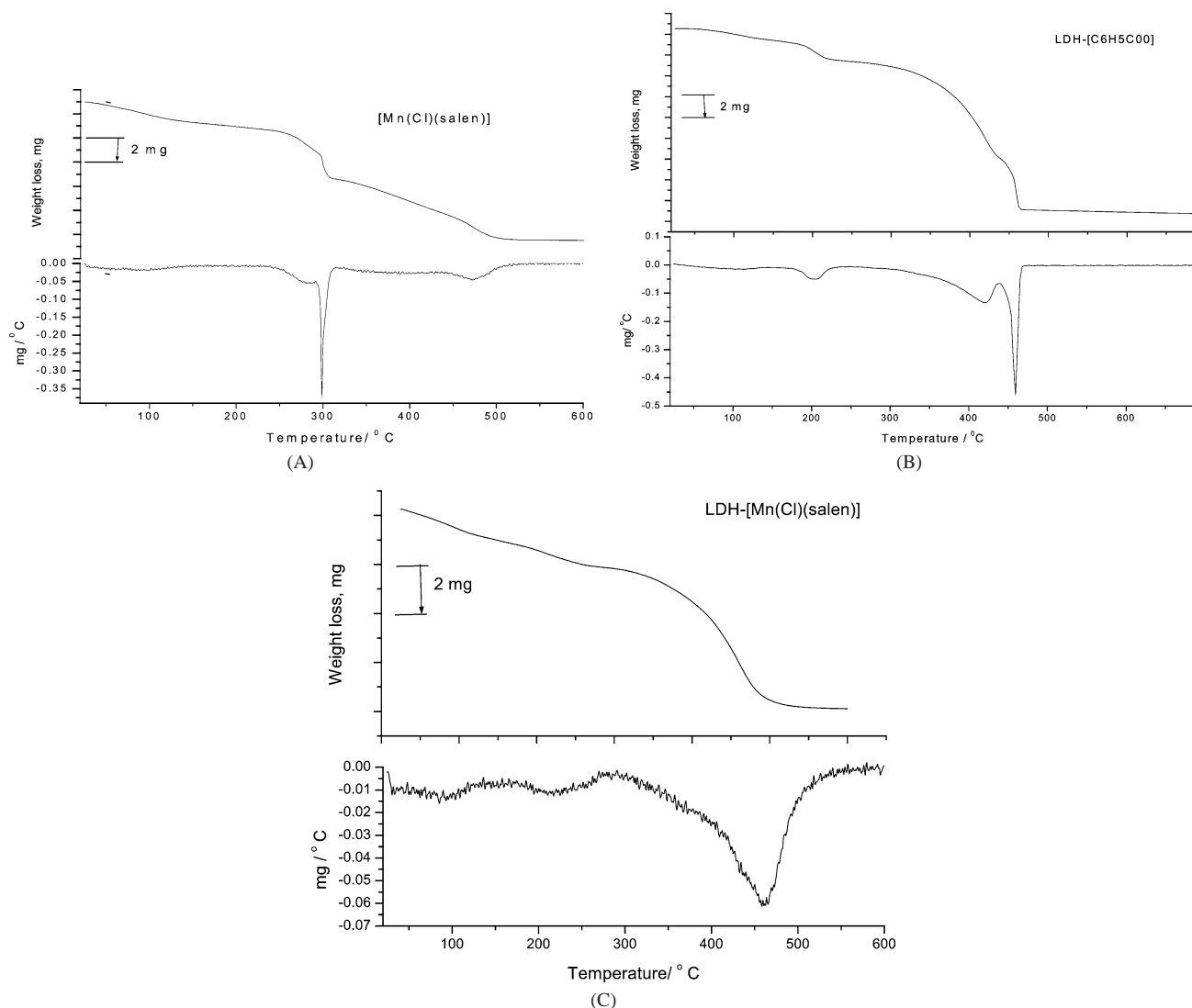


Fig. 3. TGA (upper) and first derivative curves (lower) of (A)  $\text{Na}_2[\text{Mn}(\text{Cl})(\text{L})]$ , (B)  $\text{LDH}[\text{C}_6\text{H}_5\text{COO}]$ , and (C)  $\text{LDH}[\text{Mn}(\text{Cl})(\text{L})]$ .

the energy level diagram is as in Fig. 4, which dictates the occurrence of three d–d transitions assignable to  ${}^5\text{B}_2 \leftarrow {}^5\text{B}_1$ ,  ${}^5\text{A}_1 \leftarrow {}^5\text{B}_1$  and  ${}^5\text{E} \leftarrow {}^5\text{B}_1$  [33]. The electronic spectra (Fig. 5) 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 transitions  ${}^5\text{B}_2 \leftarrow {}^5\text{B}_1$  and  ${}^5\text{A}_1 \leftarrow {}^5\text{B}_1$  [33,35]. The UV–visible spectrum of catalyst 6 (in Nujol mull) showed similar features (Table 1) to the free complex, indicating that following intercalation, no change to the manganese (III) coordination centre took place.

#### 3.4. Structure calculation of $[\text{Mn}(\text{L})(\text{Cl})]^{2-}$ and $\text{LDH}[\text{Mn}(\text{Cl})(\text{L})]$

A projection view of the  $[\text{Mn}(\text{L})(\text{Cl})]^{2-}$  ion from the B3-LYP/LanL2DZ calculation is shown in Fig. 6. This calculation revealed that the dimension of the free manganese(III) complex is ca. 17–18 Å. The calculated dimension of

chloro[*N,N'*-bis(salicylidene)-cyclohexanediamine]-manganese(III) trapped in the cages of the synthetic zeolite EMT is claimed to be 13.0 Å [34]. This structure is significantly distorted at the Mn(III) centre, and presumably results from a computer-generated fit of the complex into the zeolite host. By contrast, the published crystal structure of chloro-(1*R*,2*R*)-(–)-(1,2-cyclohexanediamino-*N,N'*-bis(3,5-di-*t*-butyl-salicylidene))-manganese(III) [29] has dimensions which are comparable with our calculated structure.

The experimental observation from X-ray powder diffraction of the  $\text{LDH}[\text{Mn}(\text{Cl})(\text{L})]$  catalyst showed  $d = 18.78$  Å in height. The other phases can also be confirmed by the medium intensity peaks at 8.6, 13.8, and 19.7 ( $2\theta/^\circ$ ) for the product. In the case of the polyoxometalate pillared layered double hydroxides [36], the interlayer distances (observed from X-ray powder diffraction) were smaller than the numerical sum of the Keggin in diameter and the ideal thickness of the hydroxide layer due to strong interaction between the ba-

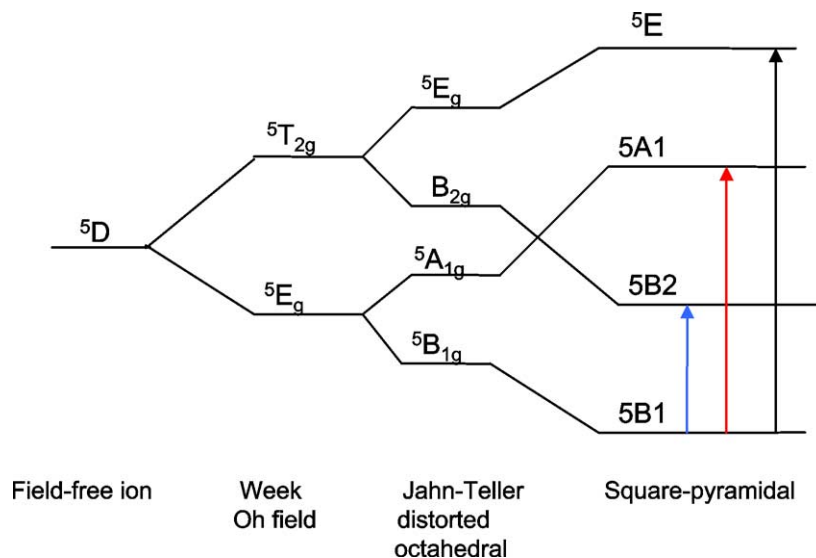


Fig. 4. Probable energy-level diagram of Mn(III) in square-pyramidal coordination.

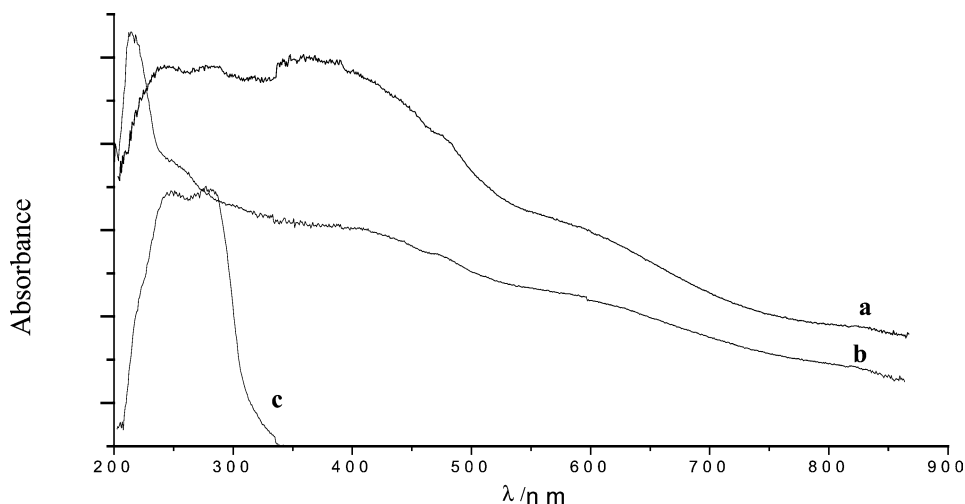


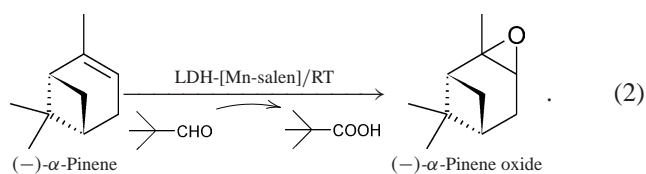
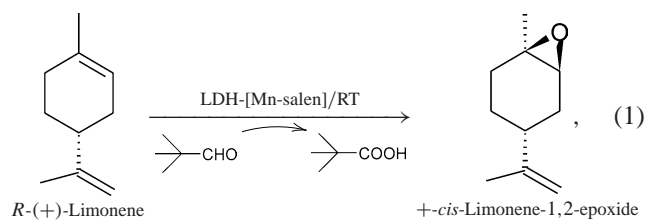
Fig. 5. UV-vis spectra of (a) LDH-[Mn(Cl)(L)], (b) free chiral sulfonato-manganese(III) complex (5) and (c) LDH-[C<sub>6</sub>H<sub>5</sub>COO] in Nujol mull.

sic layered double hydroxides and the acidic Keggin ions. In the present case, the gallery height of the LDH-[Mn(Cl)(L)] catalyst is 14.1 Å when the thickness of the brucite layers (4.7 Å) was subtracted. In a similar manner to Keggin ions in an LDH host [36], the present catalyst showed smaller *d* spacings than required to locate a perpendicularly orientated Mn complex, although it is clearly possible for the Mn complex to adopt such an orientation by penetration of the terminal sulfonato groups into the layers. Alternatively the Mn complex might be orientated either with the long axis parallel to the hydroxide layers or diagonally at an angle less than 90° to the layers.

### 3.5. 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 and also using air at atmospheric pressure (14.5

psi) and at 298 K. The reactions are expressed by Eqs. (1) and (2):



The epoxidation of (*R*)-limonene was tested at atmospheric pressure of molecular oxygen using various solvents [Eq. (1)].

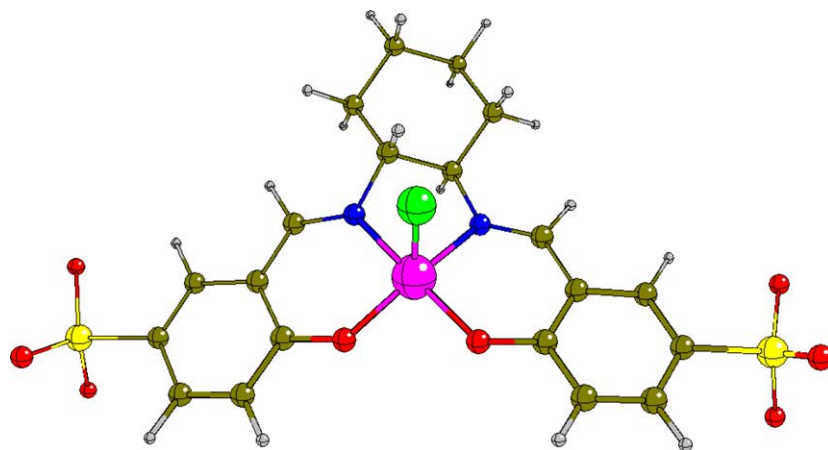


Fig. 6. Calculated structure of the sulfonato–Mn(III) salen ion (5)

Table 2  
Epoxidation of (*R*)-limonene and (–)- $\alpha$ -pinene using molecular oxygen<sup>a</sup>

Substrate	Additive	Conversion (%)	Selectivity (%)	de (%)
( <i>R</i> )-Limonene	–	96.6	88.5	33.4
( <i>R</i> )-Limonene	<i>N</i> -MeI <sup>b</sup>	94.7	93.3	42.8
(–)- $\alpha$ -Pinene	–	100.0	90.0	98.1
(–)- $\alpha$ -Pinene	<i>N</i> -MeI <sup>b</sup>	100.0	93.3	98.3

<sup>a</sup> 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.

<sup>b</sup> *N*-Methylimidazole, 1.78 mmol.

Table 3  
Influence of solvent and choice of oxidant on the epoxidation of (*R*)-limonene and (–)- $\alpha$ -pinene<sup>a</sup>

Substrate	Solvent	Oxidant	Conversion (%)	Selectivity (%)	de (%)
( <i>R</i> )-Limonene	Toluene	Dioxygen <sup>b</sup>	96.6	88.5	33.4
( <i>R</i> )-Limonene	Toluene	Air <sup>c</sup>	97.0	87.0	31.0
( <i>R</i> )-Limonene	Acetone	Air <sup>c</sup>	98.3	88.5	32.4
(–)- $\alpha$ -Pinene	Toluene	Dioxygen <sup>b</sup>	100.0	90.0	98.1
(–)- $\alpha$ -Pinene	Acetone	Air <sup>b</sup>	100.0	91.7	98.2

<sup>a</sup> Reaction conditions: 3.7 mmol substrate, 9.2 mmol pivalaldehyde, 18.5 ml solvent, 0.100 g catalyst and temperature 298 K.

<sup>b</sup> Reaction time 6 h.

<sup>c</sup> Reaction time 8 h.

The results are summarised in Tables 2–4. In toluene, 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). Addition of catalytic amounts of *N*-methylimidazole improved the de to 42.8% while the selectivity was increased to 93.3%. Yamada et al. [37] found that *N*-methylimidazole could be used to improve the ee in the epoxidation of 1,2-dihydronaphthalenes, suggesting that this axial base is capable of directing the manner in which the substrate molecule interacts with the catalyst active site. Under the above identical reaction conditions, using air as oxidant at atmospheric pressure and with toluene as solvent at 298 K, (*R*)-limonene was converted to (+)-*cis*-limonene-

Table 4  
Performance of reused catalyst in the epoxidation of (*R*)-limonene and (–)- $\alpha$ -pinene

Run	Reagent	Oxidant	Conversion (%)	Selectivity (%)	de (%)
1	( <i>R</i> )-Limonene <sup>a</sup>	Air	97	87	31
2	( <i>R</i> )-Limonene <sup>a</sup>	Air	97	89	32
3	( <i>R</i> )-Limonene <sup>a</sup>	Air	96	86	31
1	(–)- $\alpha$ -Pinene <sup>b</sup>	Oxygen	100	90.0	98.1
2	(–)- $\alpha$ -Pinene <sup>b</sup>	Oxygen	100	93.3	98.1
3	(–)- $\alpha$ -Pinene <sup>b</sup>	Oxygen	100	89.7	98.1

<sup>a</sup> Reaction conditions: 3.7 mmol (*R*)-limonene, 9.2 mmol pivalaldehyde, 18.5 ml toluene, 0.100 g catalyst and air (14.5 psi), temperature 298 K, and reaction time 8 h.

<sup>b</sup> Reaction conditions: 3.7 mmol (–)- $\alpha$ -pinene, 9.2 mmol pivalaldehyde, 18.5 ml toluene, 0.100 g catalyst, and molecular oxygen (14.5 psi), temperature 298 K, and reaction time 6 h.

1,2-epoxide with identical catalytic activity as when using molecular oxygen. Replacing the toluene by acetone and using air as oxidant, the reaction proceeded to give similar conversion, selectivity, and de (Table 3). The above observation showed that the modified Jacobsen's catalyst within the LDH host could be employed just as effectively using air or oxygen as oxidant and showed little if any dependence on the type of solvent used. The comparative data displayed in Fig. 7 show that epoxidation of (*R*)-limonene using the present LDH-based Mn–salen catalyst gave much higher selectivity using air as oxidant and acetone as solvent or using dioxygen and toluene, than those previously reported for zeolite entrapped Mn–salen [38] using fluorobenzene as solvent and high pressures of molecular oxygen, while still achieving equivalent activity and de.

The epoxidation of (–)- $\alpha$ -pinene at 298 K was also investigated using molecular oxygen or air as oxidant and using a variety of different solvents [Eq. (2)]. Under atmospheric pressure of O<sub>2</sub>, (–)- $\alpha$ -pinene was converted to (–)- $\alpha$ -pinene oxide with high conversion, selectivity, and de (Table 2). In this case, selectivity and de were not affected by the presence of the donor ligand, *N*-methylimidazole. The (–)- $\alpha$ -pinene also produced epoxide in good conver-



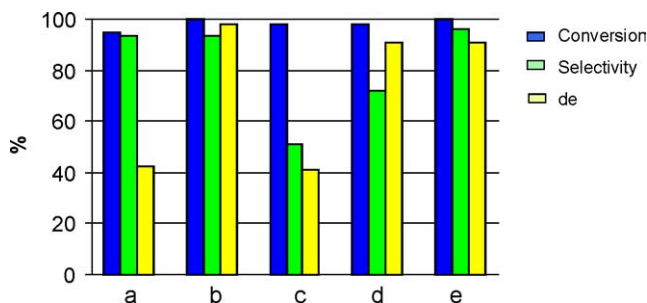


Fig. 7. Comparison of conversion, selectivity, and de (%) of (*R*)-limonene over (a) LDH hosted Mn-salen complex and (c) zeolite-immobilized Mn(salen-2) [38], and for (*-*)- $\alpha$ -pinene over (b) LDH hosted Mn-salen complex, (d) zeolite-immobilized Mn(salen-2) [38], and (e) zeolite-immobilized Co(salen) [38].

sion, selectivity, and de in the presence of acetone as solvent and using air as oxidant (Table 3), similar catalytic properties observed in (*R*)-limonene epoxidation in toluene or acetone as solvent using molecular oxygen and also in air. Using air or molecular oxygen, the conversion, selectivity, and de % were not affected by changing the solvent from toluene to acetone (Table 3). Using atmospheric pressure of either oxidant, the conversion, selectivity, and de were higher than those reported for zeolite-entrapped Mn-salen Jacobsen's catalyst [38]. An immobilized cobalt-salen complex [38] was found to produce the highest catalytic activity in a series of zeolite entrapped metal-salen systems. A comparison of data obtained for (*-*)- $\alpha$ -pinene epoxidation is shown in Fig. 7. The modified Jacobsen's catalyst shows higher conversion, selectivity, and de, when hosted in the layered double hydroxide catalyst than a zeolite-entrapped Mn-salen [38] in heterogeneous systems. A higher de but slightly lower selectivity was also found for our catalyst when compared with recently reported results for a zeolite-entrapped Co-salen catalyst [38]. The present results are at odds with the claim [38] that Jacobsen's catalyst is not particularly suited for the (*-*)- $\alpha$ -pinene epoxidation reaction, indicating that the use of the LDH as host provides some additional features to the catalytic process.

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, irrespec-

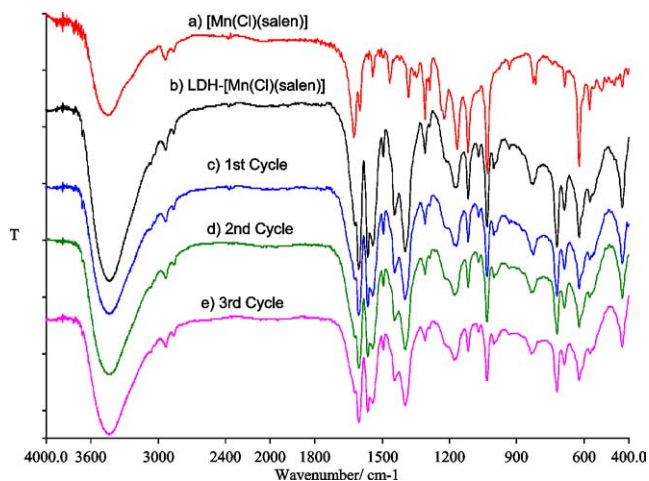


Fig. 8. IR spectra of (a) fresh Na<sub>2</sub>[Mn(Cl)(L)], (b) fresh LDH-[Mn(Cl)(L)] and LDH-[Mn(Cl)(L)] catalyst after (c) first run, (d) second run, and (e) third run.

tive 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 (Fig. 8) of the solid catalyst after reuse was also identical to the fresh catalyst.

The advantages of the present catalyst for epoxidation reactions with respect to the homogeneous Jacobsen's catalyst or anchored Mn salen systems are:

- Use of molecular oxygen or air instead of sodium hypochlorite as oxidant as used in Jacobsen's system [5]. NaOCl requires careful handling and storage considerations and, in addition to being toxic and corrosive, has the potential to release chlorine gas. Use of air or oxygen improves the atom efficiency of the overall process with respect to the use of NaOCl and avoids the formation of NaCl.
- The use of air or oxygen at atmospheric pressures overcomes the need for complex pressure vessels and additional safety features which are essential for a system operating at elevated pressures.
- The catalyst is active at room temperature using acetone or toluene as solvent instead of fluorobenzene required by others [38] to achieve good activity. The latter is an eye, skin, and respiratory irritant with potential toxicological effects.

Mechanistic studies as well as comparative studies with the use of the other transition metal-salen complexes into the layered double hydroxide in the epoxidation of different olefins as well as the use of other oxidants are in progress to understand the role of the layered double hydroxide host on the enantio- and diastereoselectivities.

#### 4. Conclusions

The chiral  $\text{SO}_3^-$  salen–Mn(III) complex intercalated into Zn/Al-LDH has been prepared and tested for its epoxidation activity using (*R*)-limonene and (–)- $\alpha$ -pinene as model compounds using air and molecular oxygen as oxidant at atmospheric pressure and at 298 K under a very mild reaction condition using acetone as a solvent. The chiral salen ligand and metal complexes synthesised in this study from aqueous medium were obtained in high yield and high purity. The LDH-[Mn(Cl)(L)] catalyst showed higher conversion, selectivity, and de % for (*R*)-limonene and (–)- $\alpha$ -pinene epoxidation when compared with other published data for other Mn–salen catalysts.

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