

# Clay-supported non-chiral and chiral Mn(salen) complexes as catalysts for olefin epoxidation

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## Abstract

Clay-supported non-chiral Mn(salen) catalysts have been prepared by two methods, direct exchange of the complex or treatment of the Mn-exchanged clay with the salen ligand. The first method, which leads to more homogeneously distributed catalysts, has been also used with a chiral Mn(salen) complex. Depending on the size and the amount of exchanged complex and the structure and surface area of the clays, the catalysts can show expanded basal spacings. All the solids promote epoxidation reactions with iodosylbenzene, reaching turnover numbers similar or higher than those obtained in solution with related catalysts. However, the supported chiral catalyst leads to a slightly lower enantioselectivity. The recovery of the catalysts leads to a reduction of activity and mainly of enantioselectivity, as in the case of the chiral catalyst, which cannot be related with leaching of complex. Spectroscopic studies indicate that the decomposition of the ligand is the main reason for this behaviour. © 1998 Elsevier Science B.V. All rights reserved.

*Keywords:* Asymmetric epoxidation; Heterogeneous catalysis; Mn(salen) on clays

## 1. Introduction

The search for new oxidation catalysts is one of the most important current topics, connected with both industrial and academic research. In this field, the use of Mn(salen) catalysts has received great attention in the last few years, given that they have shown to be useful in the asymmetric epoxidation of non-functionalized olefins [1]. Despite its interest, this method of

epoxidation suffers from some drawbacks from a practical point of view. The low turnover number, the catalyst deactivation, the high cost of the complex and the lack of recycling methods make it difficult for application of this system on a large scale.

Therefore some attempts have been made in order to support non-chiral as well as chiral Mn(salen) complexes. The encapsulation in zeolites [2–5], the grafting on polymers [6–8] or MCM-41 silica [9] and the immobilization in polysiloxane membranes [10] have been used as supporting methods, with moderate to excellent results. The cationic nature of the Mn(salen) complexes opens the way to their heterogeneiza-

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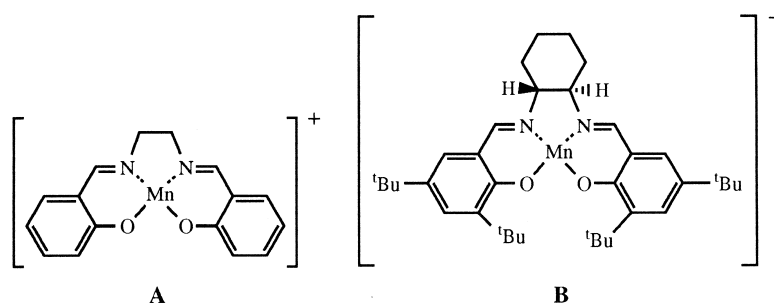


Fig. 1.

tion by a simpler method, namely the exchange in clays with cation exchange capacity. These solids have been extensively used to support porphyrines, phthalocyanines [11] and other metal-complexes [12–16]. However the only reference about their use in supporting Mn(salen) complexes deals with the use of kaolinite [17], a clay with essentially no cation exchange capacity [18].

In view of this, we decided to investigate the use of this methodology to obtain non-chiral and chiral Mn(salen) complexes (Fig. 1) supported on clays.

## 2. Experimental

Manganese (II) acetate tetrahydrate and (*R,R*)-(–)-*N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamino-manganese (III) chloride were purchased from Aldrich. Manganese (III) acetate dihydrate, cyclohexene and 1,2-dihydronaphthalene were purchased from Fluka. The non-chiral salen ligand, *N,N'*-bis(salicylidene)-ethylenediamine, was obtained in 85% yield by mixing salicylaldehyde (2 eq) and ethylenediamine (1 eq) in ethanol. Iodosylbenzene was prepared according to literature procedures [19] from diacetoxyiodobenzene (Fluka). Mn(salen) acetate was also prepared according to a literature procedure [20]. Laponite (Laporte adsorbents) was used as received. Bentonite (Fluka) and K10-montmorillonite (Aldrich) were exchanged with 1 M NaCl before use. Acetoni-

trile and pyridine were dried by means of standard methods and stored over 3 Å molecular sieves.

### 2.1. Heterogeneous non-chiral catalysts prepared by direct exchange (Method A)

5 g of the corresponding solid (Na-bentonite, Na-K10 or laponite) were slowly added to a solution of Mn(salen) acetate (see Table 1) in 125 ml of methanol and the resulting suspension was stirred at 40°C for 24 h. The brown solid was filtered, washed with methanol and dried at 50°C under vacuum.

### 2.2. Heterogeneous non-chiral catalysts prepared by exchange with Mn(II) and treatment with the salen ligand (Method B)

5 g of the corresponding solid (Na-bentonite, Na-K10 or laponite) were slowly added to a solution of manganese (II) acetate tetrahydrate (1.837 g, 7.5 mmol) in 125 ml of methanol. The suspension was stirred at room temperature for 24 h. The light brown solid was filtered, washed with methanol and dried at 50°C under vacuum. 1 g of this solid was added to a solution of the salen ligand (0.214 g, 0.8 mmol) and lithium chloride (0.064 g, 1.5 mmol) in methanol (160 ml). The suspension was heated under reflux for 24 h. The dark brown solid was filtered, washed with methanol and dried at 50°C under vacuum.

Table 1  
Results of the oxidation of cyclohexene with PhIO (0.5 eq) at room temperature with supported non-chiral Mn(salen) catalysts

Clay	Method	Mn content <sup>a</sup> (mmol g <sup>-1</sup> )	$d_{001}$ (Å)	TOF epoxidation <sup>b</sup>	Yield epoxide <sup>c</sup>	Epox/allylic <sup>d</sup>	TON <sup>e</sup>
Bentonite	A	0.18	20.1 <sup>f,g</sup>	10.1	64	83:17	6.4
	recovered	0.17	14.5	6.4	46	85:15	4.9
Bentonite	A	0.05	13.9	8.8	33	80:20	11.9
	recovered	0.05	13.8	1.3	5	63:37	1.9
Laponite	A	0.49	21.3 <sup>h</sup>	2.2	65	88:12	2.4
	recovered	0.44	17.5	2.9	42	88:12	1.7
Laponite	A	0.25	15.9	2.8	62	80:20	4.5
	recovered	0.24	16.0	1.8	62	80:20	4.5
Laponite	A	0.05	16.3	19.4	42	84:16	15.1
	recovered	0.05	16.1	1.0	7	66:34	2.4
K10	A	0.19	–	6.8	52	86:14	4.9
	recovered	0.19	–	3.6	52	87:13	4.9
K10	A	0.05	–	16.6	36	88:12	13.0
	recovered	0.05	–	1.3	6	71:29	2.1
Bentonite	B	0.33 <sup>i</sup>	20.9	4.2	56	87:13	3.1
	recovered	0.31	15.1	2.9	52	84:16	3.0
Laponite	B	0.53 <sup>j</sup>	17.2	2.6	56	92:8	1.9
	recovered	0.35	16.1	2.5	52	91:9	2.7
K10	B	0.23 <sup>k</sup>	–	6.0	53	91:9	4.1
	recovered	0.23	–	4.4	37	86:14	2.9

<sup>a</sup>The C/N and N/Mn ratios agree with the composition of the complex within the experimental error.

<sup>b</sup>mmol epoxide (mmol Mn)<sup>-1</sup> h<sup>-1</sup> from data after 30 min.

<sup>c</sup>Referred to the maximum for overall conversion of PhIO, after 2–3 h.

<sup>d</sup>epoxide/(cyclohexenol + cyclohexenone).

<sup>e</sup>mmol epoxide (mmol Mn)<sup>-1</sup>.

<sup>f</sup>Bentonite  $d_{001}$  = 13.7 Å.

<sup>g</sup>Broad signal.

<sup>h</sup>Laponite  $d_{001}$  = 16.1 Å.

<sup>i</sup>Before treatment with salen ligand the Mn content in bentonite was 0.46 mmol g<sup>-1</sup>.

<sup>j</sup>Mn content in Mn-laponite was 0.69 mmol g<sup>-1</sup>.

<sup>k</sup>Mn content in Mn-K10 was 0.35 mmol g<sup>-1</sup>.

### 2.3. Preparation of the supported chiral catalyst

A solution of the chiral Mn(salen)Cl (238 mg, 0.375 mmol) in methanol (10 ml) was added to a suspension of laponite (5 g) in methanol (100 ml). The resulting suspension was stirred at room temperature for 48 h. The brown solid was filtered, washed with methanol and extracted with acetonitrile in a Soxhlet apparatus for 72 h. The catalyst was dried at 60°C under vacuum overnight prior to use.

### 2.4. Characterization of the catalysts

Manganese analyses were carried out by plasma emission spectroscopy on a Perkin-Elmer Plasma 40 emission spectrometer. Carbon and

nitrogen analyses were carried out in a Perkin-Elmer 2400 elemental analyzer. Step-scanned X-ray diffraction patterns of oriented samples were collected at room temperature from 3° in 2θ up to 60° using a D-max Rigaku system with rotating anode. The diffractometer was operated at 40 kV and 80 mA and the CuKα radiation was selected using a graphite monochromator. Diffuse reflectance UV spectra were recorded with an Unicam UV4 spectrometer equipped with a Labsphere diffuse reflectance attachment. Infrared spectra were taken of self-supporting wafers of the catalyst samples with a Mattson Genesis Series FTIR. Thermogravimetric analyses were carried out on a TA Instruments 2000 thermal analyzer under N<sub>2</sub> flow

(10°C/min to 600°C) and then under air flow (5 min at 600°C).

### 2.5. Reactions of cyclohexene oxidation

To a solution of cyclohexene (74 mg, 0.90 mmol) and decane (internal standard) in 15 ml of acetonitrile, 250 mg of the catalyst and then 100 mg of iodosylbenzene (0.45 mmol) were added at room temperature under argon atmosphere. The reaction was monitored by gas chromatography on a Hewlett-Packard 5890II FID, cross-linked methyl silicone column 25 m × 0.2 mm × 0.33 μm, helium as a carrier gas 20 psi, oven temperature program 45°C (4 min)–25°C/min–250°C (2 min), retention times: cyclohexene 3.4 min, cyclohexene oxide 6.5 min, 2-cyclohexenol 6.9 min, 2-cyclohexenone 7.3 min, decane 8.5 min, iodobenzene 8.7 min). The assignment was made by comparison with authentic samples. After reaction the catalysts were filtered, washed with acetonitrile and dichloromethane, dried at 50°C under vacuum and analyzed. Some of them were reused in the same conditions.

### 2.6. Homogeneous asymmetric epoxidation of 1,2-dihydronaphthalene

To a solution of 1,2-dihydronaphthalene (201 mg, 1.54 mmol), chiral Mn(salen)Cl (17 mg, 0.028 mmol) and pyridine (22 mg, 0.28 mmol, when used) in acetonitrile (19 ml), iodosylbenzene (515 mg, 2.31 mmol) was added. The reaction was stirred for 24 h at room temperature, the solvent evaporated under reduced pressure and the crude analyzed by <sup>1</sup>H-NMR. The epoxide was purified by chromatography column with a home-made 'end-capped' silica [21] as the stationary phase and hexane as an eluent. The absolute configuration was determined by polarimetry ( $[\alpha]_D +135$  for the (1*R*,2*S*)-epoxide [22]). Enantiomeric excess was determined with the pure epoxide by <sup>1</sup>H-NMR in the presence of Eu(hfc)<sub>3</sub>. Optical yields determined

by polarimetry were in agreement with the enantiomeric excesses determined by <sup>1</sup>H-NMR.

### 2.7. Heterogeneous asymmetric epoxidation of 1,2-dihydronaphthalene

To a solution of 1,2-dihydronaphthalene (250 mg, 1.92 mmol) and pyridine (27 mg, 0.35 mmol, when used) in acetonitrile (24 ml), 500 mg of the supported catalyst (0.022 mmol) were added. After the addition of iodosylbenzene (640 mg, 2.88 mmol) the reaction was stirred for 24 h at room temperature. The solid catalyst was filtered and washed with dichloromethane. The solvent was evaporated under reduced pressure and the crude was analyzed by <sup>1</sup>H-NMR. The epoxide was purified as described above and the enantiomeric excess was determined by <sup>1</sup>H-NMR in the presence of Eu(hfc)<sub>3</sub>. The recovered catalyst was dried at 60°C under vacuum, analyzed and reused in the same conditions.

## 3. Results and discussion

In order to test the possibility of supporting cationic Mn(salen) complexes into clays, we studied the exchange of the non-chiral complex in three clays with different properties: a natural smectite with lamellar structure (bentonite, > 80% montmorillonite); an iron-free synthetic laponite with higher swelling ability; and an acid-treated montmorillonite (K10) with disordered structure (house-of-cards structure [23,24]). In order to have reproducible starting materials, bentonite and K10 were exchanged with NaCl 1 M, washed with deionised water and the heavy dark grey fraction discarded. The samples used in the exchange had BET surface areas of 30 m<sup>2</sup> g<sup>-1</sup> (Na-bentonite), 255 m<sup>2</sup> g<sup>-1</sup> (laponite) and 230 m<sup>2</sup> g<sup>-1</sup> (Na-K10). In the case of lamellar clays, the basal spacings were 13.7 Å (Na-bentonite) and 16.1 Å (laponite).

The first method used to obtain the supported catalysts was the direct exchange with the non-

chiral Mn(salen) acetate [20] in methanol (method A). In this way, several samples were obtained with different amounts of exchanged complex (Table 1). The highest Mn content represents the upper limit and it cannot be increased even using higher complex/clay ratios in the exchange process. In the case of the lamellar clays, low exchange levels do not produce any increase in the basal spacing, which is in turn expanded with a higher amount of exchanged complex (Table 1). This result seems to indicate that the exchange is easier on the outer surface of the clay, and only when the external sites are completely exchanged, does the complex enter between the silicate sheets. The higher swelling capacity of laponite allows a higher amount of complex enter between the sheets, and the diffraction line is quite sharp (Fig. 2). However, in the case of bentonite, a wide diffraction line is obtained (Fig. 3) which indicates a less uniform distribution of the basal spacing as a consequence of a less uniform distribution of the complex in the interlamellar zone. This behaviour may indicate that, due to the minor swelling ability of this clay, only the intralamellar sites near to the platelet edges are able to be exchanged. The N/Mn and C/N ratios were always in good agreement with the theoretical values.

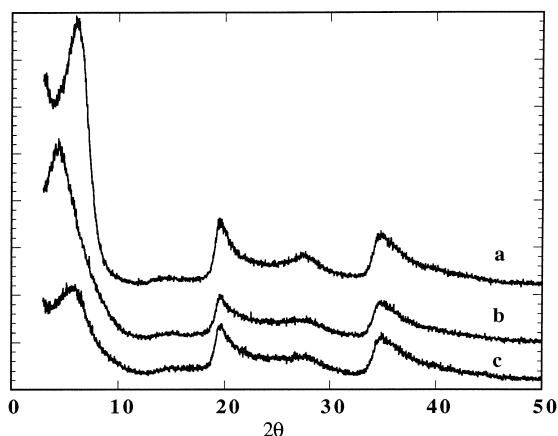


Fig. 2. DRX patterns in laponites: (a) laponite, (b) non-chiral Mn(salen)-laponite  $0.49 \text{ mmol g}^{-1}$ , (c) non-chiral Mn(salen)-laponite (method B).

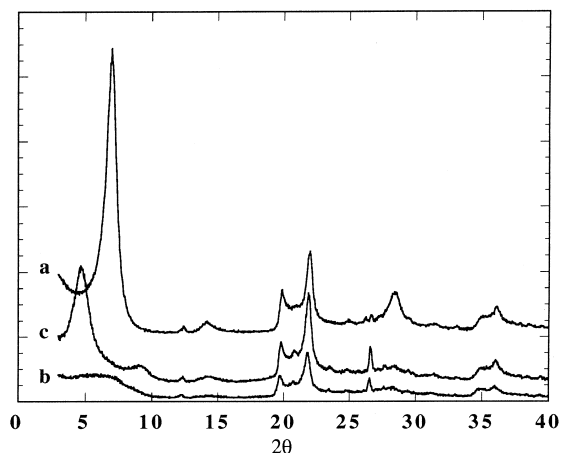


Fig. 3. DRX patterns in bentonites: (a) bentonite, (b) non-chiral Mn(salen)-bentonite  $0.18 \text{ mmol g}^{-1}$ , (c) non-chiral Mn(salen)-bentonite (method B).

In order to test a second method (method B) to prepare the supported catalysts, we exchanged the three clays with Mn(II) by a standard procedure. The solids obtained contained an amount of Mn greater than the maximum obtained by the exchange of the complex. The treatment of these clays with the potassium salt of the non-chiral salen ligand did not allow the incorporation of the ligand into the solid, which was achieved by adding LiCl to the ligand solution. The amount of exchanged complex was similar to the maximum reached with method A for laponite and K10, but it was very much higher with bentonite (Table 1). This clay showed expanded basal spacing (Fig. 3), whereas laponite, surprisingly, did not (Fig. 2). The carbon and nitrogen analyses showed the complete formation of the complex.

The comparison of both methods shows that the distribution as well as the amount of complex introduced into the solids depend on the methodology used to support it.

The identities of the exchanged complexes were confirmed by comparing their spectroscopic features with those of the non-supported complex. The diffuse reflectance UV spectra of the solids show a shape similar to that of the complex in solution, with two shoulders at 402 and 460 nm. However, a more detailed informa-

tion was obtained from the IR spectra, which show signals at  $3070$  and  $3020\text{ cm}^{-1}$  ( $\text{C}_{\text{arom}}\text{-H}$ ),  $2950$  and  $2870\text{ cm}^{-1}$  ( $\text{C}_{\text{aliph}}\text{-H}$ ) and in the region between  $1700$  and  $1200\text{ cm}^{-1}$ . In this region some differences are observed as a function of the support and the amount of supported complex. In the case of laponite with a small amount of exchanged complex (Fig. 4c), the bands at  $1618$ ,  $1602$ ,  $1548$ ,  $1471$ ,  $1448$ ,  $1388$ ,  $1332$  and  $1280$  fit well with the spectrum described for the non-chiral  $\text{Mn}(\text{salen})\text{PF}_6$  [25]. The bands at  $1618$  and  $1602\text{ cm}^{-1}$  cannot be distinguished in the samples with a greater amount of complex, where a broad band is observed (Fig. 4a,b). A similar behaviour is observed in K10-montmorillonites. However, in bentonites (Fig. 5), the broad band of the support, between  $1544$  and  $1447\text{ cm}^{-1}$ , makes the identification of the complex more difficult, but the bands at  $1620\text{--}1600$ ,  $1548$ ,  $1448$ ,  $1332$  and  $1280\text{ cm}^{-1}$  are visible in the spectra.

The catalytic activity of these clays was tested in the oxidation of cyclohexene with iodosylbenzene (Scheme 1), and the results are gathered in Table 1.

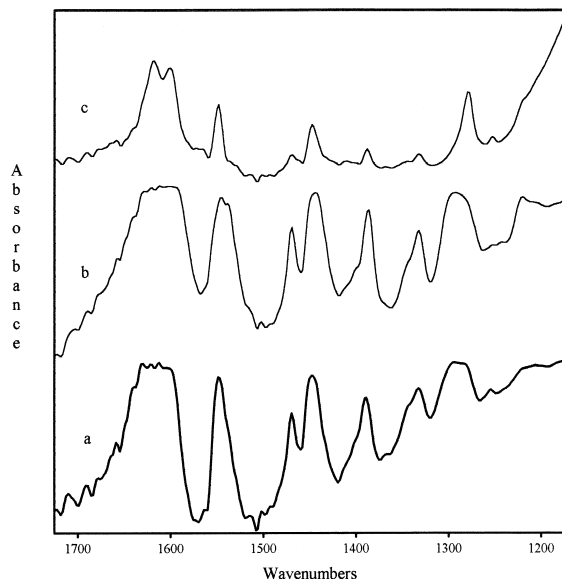


Fig. 4. IR spectra of laponite samples with non-chiral  $\text{Mn}(\text{salen})$  dried at  $120^\circ\text{C}$ : (a)  $0.49\text{ mmol g}^{-1}$ , (b) method B, (c)  $0.05\text{ mmol g}^{-1}$ .

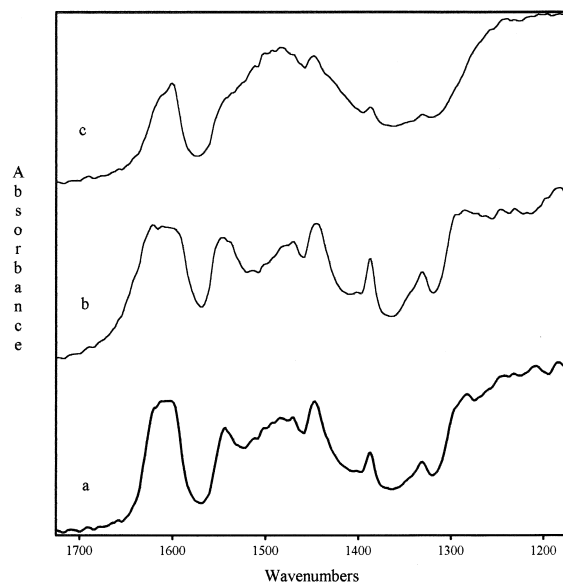
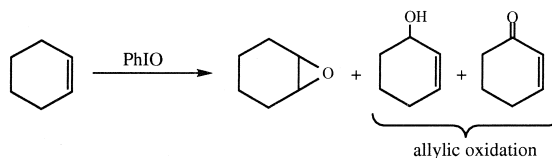


Fig. 5. IR spectra of bentonite samples with non-chiral  $\text{Mn}(\text{salen})$  dried at  $120^\circ\text{C}$ : (a)  $0.18\text{ mmol g}^{-1}$ , (b) method B, (c)  $0.05\text{ mmol g}^{-1}$ .

First of all, it is important to note that the catalytic activity is another confirmation of the structural identity of the complex on the clays, given the very low activity of the clays which were exchanged with  $\text{Mn}(\text{II})$  (yield in epoxide  $\leq 4\%$ ). Except with the solids with a very low content of complex, the freshly prepared catalysts lead to about 60% yield in epoxide. The catalytic activity per manganese increases when the amount of exchanged complex is reduced, indicating a lower activity of the crowded and/or the interlamellar molecules, which is probably due to diffusional restrictions [26]. In order to find the maximum TON, we carried out the reaction with a bentonite ( $0.18\text{ mmol Mn g}^{-1}$ ), a laponite ( $0.25\text{ mmol Mn g}^{-1}$ ) and a K10 ( $0.19\text{ mmol Mn g}^{-1}$ ), using  $250\text{ mg catalyst}/4.5\text{ mmol PhIO}/9\text{ mmol cyclohexene}$ . A



Scheme 1.

complete oxidant conversion was observed after 48 h and the TON values were 38.8, 43.2 and 40.9 respectively. These values are higher than the TON described for the homogeneous catalyst [27] and similar to those reported for chiral complexes [28].

After the reaction all the catalysts were separated by filtration, thoroughly washed and reused in the same conditions. The analyses of the recovered catalysts show that there is no loss of manganese, except in the laponite prepared by method B. In general, the recovered catalysts show a slightly lower catalytic activity, but in the solids bearing a small amount of complex, the activity is noticeably reduced. The solids with expanded basal spacing lose it after the reaction, which may be due to the mobility of the complex or to a partial destruction of the lamellar structure. The lower intensity of the diffraction lines agree with the later hypothesis (Fig. 6).

The comparison between the two methods used to obtain the catalysts shows that preparations using method A lead to slightly better results.

In view of these results, we decided to test the possibility of supporting a chiral complex (Fig. 1B). As support, we selected laponite because of its higher surface area and swelling

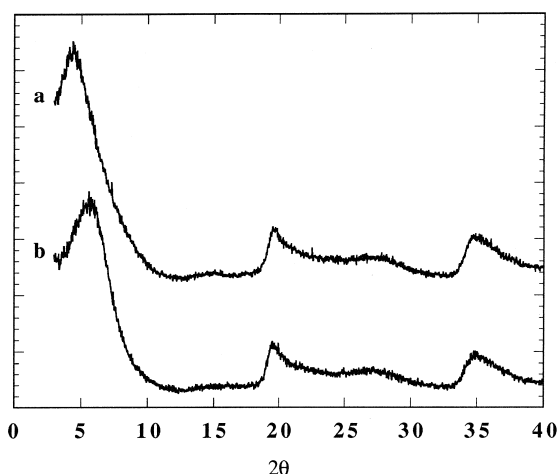


Fig. 6. DRX patterns of the laponite ( $0.49 \text{ mmol g}^{-1}$ ) (a) before and (b) after the reaction.

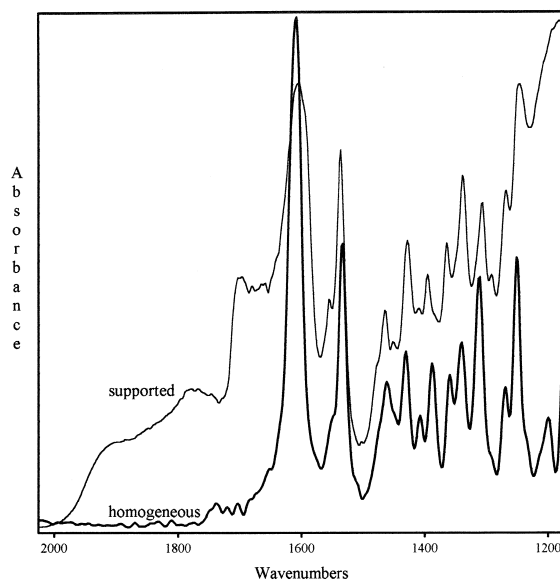
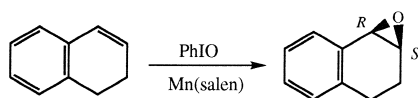


Fig. 7. IR spectra of the supported and non-supported chiral Mn(salen) complex.

ability in comparison with bentonite, and its lower acidity in comparison with K10. In fact, a very acidic support can promote side reactions of the reagent, 1,2-dihydronaphthalene, or the resulting epoxide. The chiral complex was supported by direct cation exchange in methanol with the previously formed complex. After filtering and washing, the clay was extracted with acetonitrile in a Soxhlet apparatus in order to remove the physisorbed complex. The identity of the supported complex was again determined by comparison of its IR spectrum with that of the initial complex (Fig. 7). The solid obtained in this way contains  $0.044 \text{ mmol Mn g}^{-1}$  and does not show expanded basal spacing. The larger size of the chiral complex diminishes the exchangeable amount and precludes the intercalation.

Given that this chiral complex had been only used with NaClO as an oxidant [29,30], and given that these conditions are not suitable for a clay-supported cationic complex, we compared the homogeneous and the heterogeneous catalysts in the epoxidation of 1,2-dihydronaphthalene with iodobenzene (Scheme 2). It has been described that the presence of axial lig-



Scheme 2.

ands, such as pyridine, modifies both the activity [25] and the enantioselectivity [31] of metal-salen catalyzed epoxidations. In view of this, the effect of pyridine both on homogeneous and heterogeneous reactions was also tested. To determine the asymmetric induction, the epoxide was purified by column chromatography. Attempts to use silica gel and neutral alumina as the stationary phase were unsuccessful and only products coming from opening and rearrangement of the epoxide were isolated. The pure epoxide was obtained using a home-made 'end-capped' silica as the stationary phase [21]. In all the cases, the efficiency of the column that was referred to the recovery of the epoxide was ca. 90%. The difference between conversion of dihydronaphthalene and yield of epoxide was due to the formation of naphthalene under the reaction conditions.

The results obtained in the asymmetric epoxidation of 1,2-dihydronaphthalene are gathered in Table 2. As it can be seen, the turnover numbers obtained with the homogeneous and supported catalysts are quite similar. However, in the absence of pyridine, the enantiomeric

excess is lower than the heterogeneous catalyst. The addition of pyridine as an axial ligand reduces the asymmetric induction in the homogeneous reaction, but it has no significant effect on the supported catalyst. These results suggest that the clay is not merely a spectator, and that some interaction support-complex exists. It may be speculated that the clay acts as an axial ligand.

The recovered catalysts show a slight decrease of Mn content, but this decrease is not very significant given the adsorption of organic products, as shown by the higher carbon content; however, the N/Mn ratio remains constant. As observed with the clays with low content of non-chiral complex, the Mn in the recovered catalysts is much less active as shown by the lower turnover number. Furthermore, the ability of the catalysts to induce asymmetry is also reduced. It is important to note that the reduction of the asymmetric induction does not seem to be related to a particular support or oxidant. In fact, a similar loss of enantioselectivity has been also observed by Ogunwumi and Bein [5] using a zeolite as a support and NaClO as an oxidant.

Given the absence of leaching and the constant N/Mn ratio, it may be thought that the ligand is modified during the reaction, and this is the main reason for the deactivation of the catalyst. In fact, a similar explanation has been

Table 2

Results obtained in the asymmetric epoxidation of 1,2-dihydronaphthalene with iodosylbenzene in acetonitrile

Clay	Axial ligand	Reaction	Conversion <sup>a</sup>	Yield epoxide <sup>a</sup>	TON <sup>b</sup>	% e.e. <sup>c</sup>
—	—	—	100	70	38.5	46
Laponite	—	1	66	45	39.3	32
Laponite	—	2 <sup>d</sup>	20	14	14.5	28
—	pyridine	—	100	74	40.7	36
Laponite	pyridine	1	77	56	48.9	34
Laponite	pyridine	2 <sup>e</sup>	31	18	18.1	1

<sup>a</sup>Determined by <sup>1</sup>H-NMR.

<sup>b</sup>mmol epoxide (mmol Mn)<sup>-1</sup>.

<sup>c</sup>Determined by <sup>1</sup>H-NMR in the presence of Eu(hfc)<sub>3</sub>. The absolute configuration of the major (1*R*,2*S*)-epoxide was determined by polarimetry.

<sup>d</sup>The recovered clay contains 0.037 mmol Mn g<sup>-1</sup>.

<sup>e</sup>The recovered clay contains 0.039 mmol Mn g<sup>-1</sup>.



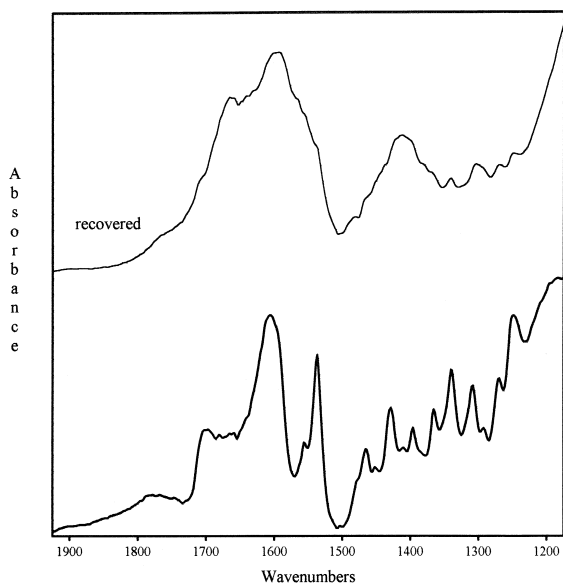


Fig. 8. IR spectra of the supported chiral Mn(salen) complex before and after the reaction.

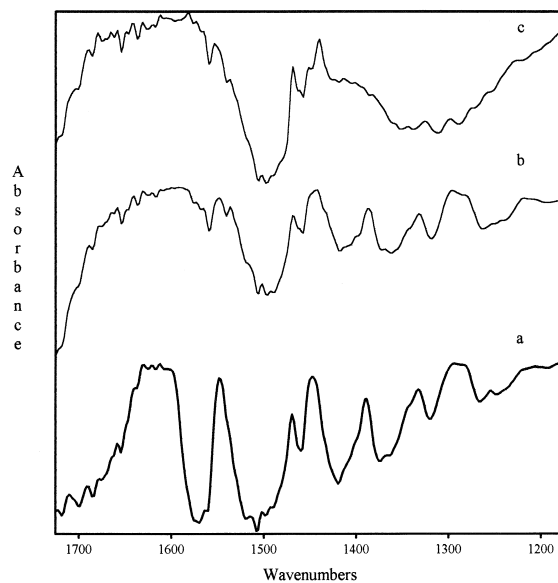


Fig. 9. IR spectra of non-chiral Mn(salen) on laponite ( $0.49 \text{ mmol g}^{-1}$ ): (a) as prepared, (b) used once, (c) used five times.

proposed for the irreversible modification of (salen)Cr = O in solution [32]. In order to test this hypothesis, we carried out different experiments. First of all, the clay-supported catalyst was ‘aged’ by treatment with iodobenzene for 24 h, and after filtration, the resulting solid was tested as catalyst in the reaction of 1,2-dihydronaphthalene with iodobenzene. In that case, 29% yield of racemic epoxide was obtained. The yield of epoxide agrees with the presence of some kind of manganese complex, but the lack of enantioselectivity shows that the complex is not the original one. The comparison of the IR spectra of the catalyst before and after

the reaction agrees with this change in the structure of the complex (Fig. 8). The recovered catalyst shows a broadening of the signals with an increase in the relative intensity of the bands at  $1666$  and  $1414 \text{ cm}^{-1}$  and a decrease of the band at  $1537 \text{ cm}^{-1}$ . Furthermore, the intensity of the signals between  $1400$  and  $1200 \text{ cm}^{-1}$  is also noticeably reduced.

Finally, we decided to test if the non-chiral complex shows a similar behaviour. We used for this proposal the laponite with the highest content of complex. The catalyst was recovered and reused four times and the results are gathered in Table 3. As it can be seen, there was no

Table 3

Recovering of non-chiral Mn(salen) complex supported in laponite with  $0.49 \text{ mmol Mn g}^{-1}$

Run	Elemental analysis ( $\text{mmol g}^{-1}$ )					TOF epoxidation	Yield epoxide	Epoxide allylic	Total TON epoxide
	Mn	C	N	C/N <sup>a</sup>	N/Mn <sup>b</sup>				
1	0.49	7.09	0.91	7.8	1.9	2.2	65	7.0	2.0
2	0.44	8.57	0.89	9.6	2.0	2.9	42	7.0	1.7
3	0.42	8.67	0.84	10.3	2.0	2.8	40	6.7	1.7
4	0.37	9.12	0.82	11.1	2.2	1.4	22	5.5	1.1
5	0.39	9.16	0.79	11.6	2.0	0.9	15	3.3	0.7

<sup>a</sup>Theoretical value 8.0.

<sup>b</sup>Theoretical value 2.0.

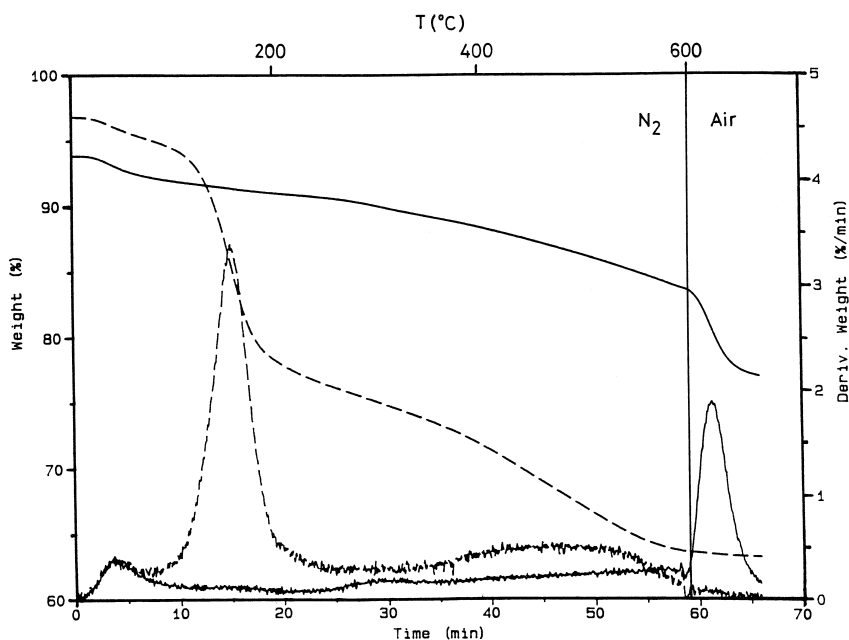


Fig. 10. Weight lost and its derivative (thermogravimetry) of non-chiral Mn(salen) on laponite ( $0.49 \text{ mmol g}^{-1}$ ) as prepared (solid line) and used five times (dashed line).

significant loss of complex and the N/Mn ratio remained constant. However, the catalytic activity, the yield of epoxide and the epoxidation/allylic oxidation selectivity were reduced after each recovery and mainly in the last recycle. Fig. 9 shows the main features of the IR spectra of the fresh catalyst, after the first reaction, and the final catalyst after five reactions. The comparison of these spectra reveals a behaviour similar to that observed with the chiral catalyst, with a reduction of the relative intensity of the band at  $1548 \text{ cm}^{-1}$ , a general broadening of the bands in the zone between  $1700$  and  $1350 \text{ cm}^{-1}$ , and the final disparition of the bands between  $1350$  and  $1250 \text{ cm}^{-1}$ , which corresponds to the ethylene bridge.<sup>2</sup> These facts show the gradual decomposition of the salen ligand, probably by oxidation. Furthermore, the band at  $2950 \text{ cm}^{-1}$  increases, which could be due to the deposition of coke coming from cyclohexene, and this

agrees with the increase in the carbon content in the recovered catalysts (Table 3).

Further confirmation of the decomposition of the salen ligand was obtained from thermogravimetric analysis (Fig. 10). The laponite sample with the highest complex content shows a slow and continuous loss of weight (8%) from 100 to  $600^\circ\text{C}$  (10–60 min) with a broad maximum at  $330^\circ\text{C}$ . The air flow at  $600^\circ\text{C}$  (60–65 min) produces the combustion of the remaining organic part (6%). The sample which was used five times shows an important loss of weight at only  $190^\circ\text{C}$  (16%) with a gradual and slow loss until  $600^\circ\text{C}$ . In this case, the air flow does not produce any combustion. This data shows the decomposition of the salen ligand, probably by partial oxidation under the reaction conditions.

#### 4. Conclusions

Non-chiral and chiral Mn(salen) complexes can be supported by direct exchange on different clays. The characteristics of the different

<sup>2</sup> During the preparation of this manuscript a similar behaviour in homogeneous Mn(salen) catalysts has been reported [33].

supports influence the amount and distribution of the complex on the surface. In all the cases, the supported Mn(salen) catalysts are active in the epoxidation of alkenes with iodobenzene as oxidant. The maximum turnover number of most of the supported catalysts is similar or higher than those obtained with the homogeneous complexes and the enantiomeric excess reached with the chiral catalyst is only slightly lower than that reached under homogeneous conditions, which is probably due to the role of the support as an axial ligand. The main limitation of Mn(salen) catalysts is their deactivation. The use of clay-supported catalysts does not completely solve the problem. Furthermore, the recovered chiral catalyst leads to very low enantioselectivity. The study of the deactivated samples reveals that the leaching of the complex is not the main reason for the loss of catalytic activity, which may be in part due to coke deposition and, above all, to the decomposition of the salen ligand, which seems to be a general limitation of this type of catalysts.

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