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Encapsulation of chiral Mn(III) *salen* complexes into aluminium pillared clays: Application as heterogeneous catalysts in the epoxidation of styrene

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Abstract

Two chiral manganese(III) *salen* complexes bearing different chiral diimine bridges, complexes **I** and **II**, were encapsulated into three types of Al-pillared clays (Al-PILCs) by in situ generation of the complexes inside the PILCs; one of the PILCs used was derived from a Wyoming clay (Al-WYO) and the other two were from the same original clay Benavila: (i) Al-BEN, where no surfactant was used in the preparation and (ii) Al-TERG, where a polyalchol, i.e. tergitol was used as surfactant to act as an interlayer gallery template. The Al-pillared clay based materials were characterised by different techniques such as FTIR, UV–vis, AA, XPS, XRD and N_2 adsorption at 77 K. They were screened as heterogeneous catalysts in the epoxidation of styrene using iodosylbenzene or *m*-chloroperbenzoic acid as oxidants. The encapsulated complexes show, in general, moderate alkene conversion (16–40%), but very poor enantiomeric excesses (ee% = 0–14); nevertheless, for complex **I** encapsulated into Al-TERG using PhIO as oxidant 14 ee% was obtained, which is higher than the value found for the homogeneous phase reaction run under comparable conditions. Characterisation of the catalyst materials after two run suggests partial collapsing of the clay pillars.

Keywords: Mn(III) *salen* complexes; Aluminium-pillared clays; Asymmetric epoxidation

1. Introduction

Asymmetric epoxidation of alkenes is a powerful strategy for the synthesis of chiral intermediates in the pharmaceutical as well as in the agrochemical industries. Chiral manganese(III) *salen* complexes were reported to be excellent catalyst for such reactions in homogeneous phase [1]. Compared to the homogeneous counterparts, heterogeneous systems have the inherent advantages of easy separation, better handling properties, as well as higher stability; therefore, heterogenisation of such complexes has been receiving recently great attention. Various approaches of immobilisation of chiral Mn(III) *salen* complexes have been reported, e.g. grafting the catalyst on solid inorganic support such as silica [2] or MCM-41 [3], encapsulation into the pores of zeolites [4], physical entrapment in a polydimethylsiloxane membrane [5], polymer support [6], clays [7] and activated carbon [8]. Excellent review articles on heterogenisation of chiral manganese(III) *salen* complexes have appeared in literature recently [9]. However, the encapsulation of the homogenous catalyst into the pores of a solid support has the advantage of being a simpler method than the grafting and anchoring approaches onto insoluble supports, which often require more complicated synthetic manipulations and structure modification of the homogeneous catalyst and lead, in general, to a decrease in the catalytic efficiency.

Pillared interlayered clays (PILCs) are two-dimensional zeolite like materials prepared by exchanging the native cations present in the interlamellar space of the parent clay with hydroxyl-metal polycations obtained from metallic salt hydrolysis [10]. Among different polycations, the Al-polycation, $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ is the most extensively studied

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because of its relatively easy way of preparation and variety of catalytic applications [11]. On calcining, the inserted polycations are transformed into metal oxide clusters by dehydration and dehydroxylation processes. These metal oxides clusters, called pillars, are inserted between the clay layers thus preventing their collapse and developing a porous network with molecular range dimensions [12]. These porous materials have the potentiality to host large molecular complexes into the interlayer region without disturbing the structure of the complexes, which is an important clue for using them as supports for heterogeneous catalysis. Besides of the immobilisation of metalloporphyrins, metallophthalocyanines [13] and molybdenum complexes [14] on PILCs and of our studies on the encapsulation of Schiff base transition metal complexes into several PILCs [15–17], little work has been reported in this field. In recent years PILCs have been attracting considerable attention as support materials mainly for several transition metal cations, that may be part of the pillars and which increase the PILC Brönsted acidity, allowing their use in heterogeneous redox catalysis [18,19]. Furthermore, and with the objective of producing PILCs with pores of large dimensions, the use of polyalcohols in the preparation of PILCs was considered [17]. More recently, we have also reported the heterogeneous catalytic activity of non-chiral manganese(III) *salen* complexes encapsulated into an aluminium-pillared montmorillonite by the in situ and simultaneous pillaring/encapsulation procedures, which have acted as selective and reusable heterogeneous catalysts [20–22]. Herein, we extend our studies to their chiral counterparts, and to the best of our knowledge, this is the first report on the encapsulation of chiral manganese(III) *salen* complexes (Fig. 1) into Al-PILCs. In this study an original clay from Benavila (a village in Portugal near where the clay was obtained) and another clay from Wyoming (USA) were used, which have the advantage of being readily available and inexpensive materials. The several pillared clays used have different structural properties, as shown by their different surface areas and pore dimensions, and it is our ultimate goal to evaluate the influence of their structural properties in the asymmetric induction of the encapsulated chiral complexes towards a standard alkene epoxidation reaction. In order to get information on the encapsulated complexes, the PILC based materials were characterised by different techniques like FTIR, UV–vis, XRD, AA, N_2-adsorption isotherms and they were screened as heterogeneous catalysts for the enantioselective epoxidation of styrene by using two different oxidant: iodosylbenzene and *m*-chloroperoxybenzoic acid.

2. Experimental

2.1. Materials

All the solvents used were purchased from Merck (grade *pro analyst*) except acetonitrile and dichloromethane used in the catalytic experiments, which were from Romil (HPLC grade). The reagents were all from Aldrich. Iodosylbenzene was synthesised according to a procedure described in the literature [3e].

2.2. Preparation of the aluminium-pillared clays

Two smectites were used as parent materials: one from Wyoming (WYO) and one from a Portuguese soil deposit in Benavila (BEN), which have been extensively characterised in previous reports [16,23]. Their structural formulae are, respectively: $(Si_{3.91}Al_{0.09})^{IV}(Al_{1.51}Fe_{0.18}Mg_{0.26})^{VI}(_{1/2}Ca,K,Na)_{0.49}$ and $(Si_{3.77}Al_{0.23})^{IV}(Al_{1.13}Fe_{0.47}Mg_{0.50})^{VI}(1/2Ca,K,Na)_{0.46}$. Their A_{BET} are 67 and 49 $m^2\,g^{-1}$, respectively, and the micropore volumes for both parent clays are very low (0.009 $cm^3\,g^{-1}$).

The PILCs, Al-WYO and Al-BEN, were prepared by using an aluminium oligomeric solution made from $AlCl_3$ and NaOH by following a procedure previously described elsewhere [16,23]. After washing and freeze drying the solid materials, they were calcined at 350 °C. The PILC Al-TERG was prepared from the parent BEN clay using an oligomer solution obtained as in the pillaring of Al-BEN or Al-WYO. However, before adding the oligomer, the clay was dispersed in a solution of polyethylene oxide (Tergitol) in water, in a ratio of 3 g of Tergitol per gram of clay, as described in detail in a previous paper by us [17].

2.3. Synthesis of chiral Schiff base ligands and respective Mn(III) complexes

The chiral Schiff base ligands, (*1R*,2*R*)-*N*,*N*′-*bis*(3,5-di-*tert*-butylsalicylidene)cyclohexanediamine, H_2(3,5-dtButsalhd), and (1*R*,2*R*)-*N*,*N*′-*bis*(3,5-di-*tert*-butylsalicylidene)diphenylethanediamine, H_2(3,5-dtButsaldPh), and the corresponding manganese(III) complexes, denoted as **I** and **II**, respectively (Fig. 1) were prepared following general methods described in the literature [8b].

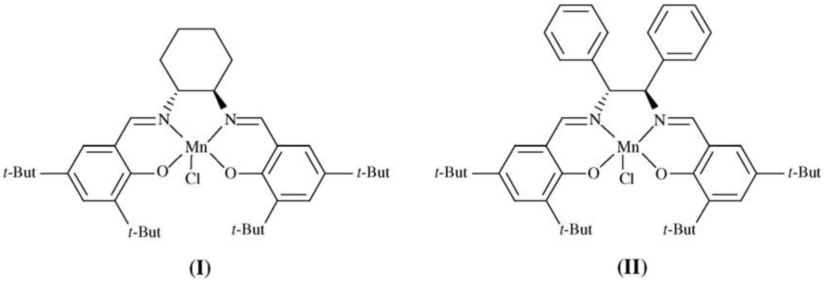

Fig. 1. Molecular structure of the Mn(III) *salen* complexes: (**I**) (1*R*,2*R*)-[Mn(3,5-dtButsalhd)Cl] and (**II**) (1*R*,2*R*)-[Mn(3,5-dtButsaldPh)Cl].

2.4. Encapsulation of complexes into the aluminium-pillared clays

The encapsulation of the two chiral manganese(III) *salen* complexes (Fig. 1) into the three materials (Al-WYO, Al-BEN and Al-TERG) was done by the in situ synthesis method [15,17,20,23] which involves a two step procedure: (i) 1.0 g of previously dried PILC was added to a solution of 0.036 g (0.18 mmol) of $MnCl_2 \cdot 4H_2O$ in 100 cm^3 of methanol and the resulting suspension was refluxed for 6 h. After filtration, the obtained residue was washed several times with methanol and then dried overnight at 120 °C, under vacuum. (ii) Then, to 1.0 g of this previously dried material, it was added a solution of 0.1 g (0.18 mmol) of Schiff base ligand H_2(3,5-dtButsalhd), or 0.1 g (0.16 mmol) of ligand H_2(3,5-dtButsaldPh) in 100 cm^3 of dichloromethane. After refluxing the reaction mixture for 6 h, it was filtered and the new materials washed several times with dichloromethane and refluxed with this solvent in order to remove residual reactants or complexes physically adsorbed on the external surface of the material. The resultant materials, denoted as **I**@Al-WYO, **I**@Al-BEN, **II**@Al-BEN, **I**@Al-TERG and **II**@Al-TERG, were then dried overnight at 120 °C.

2.5. Characterisation methods

FTIR spectra were recorded in KBr pellets in the range 400–4000 cm^{-1} using a Jasco FTIR-460 Plus spectrophotometer. Diffuse reflectance spectra were recorded on a Shimadzu UV-3101 PC spectrophotometer in the range 1500–200 nm using $BaSO_4$ as reference. The manganese contents of the PILC materials were determined by Atomic Absorption Spectroscopy using a PYE UNICAM SP9 spectrometer, after solubilisation of the samples in an autoclave with a mixture of HF and *aqua regia*.

X-ray photoelectron spectroscopy was obtained at “Centro de Materiais da Universidade do Porto” in a VG Scientific ESCALAB 200A spectrometer using a non-monochromatised Mg Kα radiation (1253.6 eV). XPS studies were performed by compressing the materials into pellets. In order to correct for possible deviations caused by electric charge of the samples, the C 1s line at 285.0 eV was taken as internal standard.

Powder X-ray diffractograms were obtained with oriented mounts on a Philips PX 1820 diffractometer using Cu Kα radiation.

Nitrogen adsorption experiments were performed at −196 °C using an automatic apparatus (ASAP 2010). Prior to the adsorption measurements the samples were outgassed at 150 °C for 2.5 h under vacuum ($p < 10^{-2}$ Pa). The isotherms were analysed by different methods, B.E.T. equation and *t*-method [24], in order to evaluate, respectively, the specific surface area, A_{BET}, and, the micropore volume, V_{micro}, of the samples.

2.6. Catalytic experiments

The catalytic activity of the Al-WYO, Al-BEN and Al-TERG based materials was evaluated at 0 °C and atmospheric pressure in batch regimen by using two different oxidant systems: iodosylbenzene (PhIO) and a mixture of *m*-chloroperoxybenzoic acid (*m*-CPBA) and *N*-methylmorpholine (NMO) as co-oxidant.

In the experiments using PhIO as oxygen source, 0.2 mmol of styrene, 0.2 mmol of chlorobenzene (GC internal standard), 0.1 g of heterogeneous catalyst and 0.1 mmol of PhIO were used in 5.00 cm^3 of acetonitrile, under stirred conditions. While the reaction was going on, time to time 0.1 cm^3 of aliquots were withdrawn from the solution with a hypodermic syringe, filtered through 0.2 μm syringe filter and analysed by GC-FID. When all the PhIO had disappeared from the reaction mixture and the ratio of iodobenzene (PhI) and chlorobenzene in the chromatogram was constant, the solution was separated by centrifugation and the supernatant liquid was transferred to another flask to which the same amount of PhIO was added and kept under stirring conditions for further 24 h, after which the solution was analysed by GC in order to investigate if there was any active phase leaching. After each utilisation, the catalyst was washed/centrifuged with methanol (five times) and with acetonitrile (two times) to remove occluded reactants and products. After drying the recovered catalyst at 100 °C in an oven overnight, they were used in another experiment under identical experimental conditions.

In the experiments using *m*-CPBA/NMO as oxidising system, 0.2 mmol of styrene, 0.2 mmol of chlorobenzene, 0.1 g of catalyst, 0.4 mmol of *m*-CPBA and 1.0 mmol of NMO in 5.00 cm^3 of dichloromethane, under stirring conditions. After 4 h of reaction the same procedure as described above for the experiment with PhIO for leaching and reuse experiment was used.

The product analysis of the catalytic experiments was done by GC-FID analysis (using the internal standard method) on a Varian CP-3380 gas chromatograph, using helium as carrier gas, equipped with a fused silica Varian Chrompack capillary column CP-Sil 8 CB Low Bleed/MS (30 m × 0.25 mm i.d.; 0.25 μm film thickness). The enantiomeric excesses percentage (ee%) of the epoxides were determined using the same chromatograph, but using a fused silica Varian Chrompack capillary column CP-Chiralsil-Dex CB (25 m × 0.25 mm i.d. × 0.25 μm film thickness). Conditions used: 60 °C (3 min), 5 °C min^{-1}, 170 °C (2 min), 20 °C min^{-1}, 200 °C (10 min); injector temperature, 200 °C; detector temperature, 300 °C. The reaction parameters %*C*, TON, TOF and ee% were calculated using the following formula, where *A* stands for area of chromatographic peak: $\%C = \{[A(\text{alkene})/A(\text{chlorobenzene})]_{t=0\,\text{h}} - [A(\text{alkene})/A(\text{chlorobenzene})]_{t=x\,\text{h}}\} \times 100/[A(\text{alkene})/A(\text{chlorobenzene})]_{t=0\,\text{h}}$; TON = mmol of converted alkene/mmol Mn; TOF = TON/time of reaction; and $\text{ee}\% = [A(\text{major enantiomer}) - A(\text{minor enantiomer})] \times 100/[A(\text{major enantiomer}) + A(\text{minor enantiomer})]$.

3. Results and discussion

3.1. Characterisation of the PILC materials

The parent PILCs (Al-WYO, Al-BEN and Al-TERG) show, as can be seen from Table 1, very similar basal spacing values (d_{001}), that is, quite comparable gallery heights. The specific surface area of Al-WYO is the lowest and, for the other two PILCs, although the total (micro plus meso) pore volumes are similar, the proportion of mesopores is highest for Al-TERG, as

Table 1
Basal spacing (d_{001}) and textural properties for the PILC materials

Sample	d_{001} (nm)	A_{BET} ($\text{m}^2\ \text{g}^{-1}$)	V_{micro} ($\text{cm}^3\ \text{g}^{-1}$)	V_{meso} ($\text{cm}^3\ \text{g}^{-1}$)
Al-WYO	1.81	196	0.07	0.06
I@Al-WYO	1.81	149	0.05	0.06
Al-BEN	1.81	338	0.14	0.04
I@Al-BEN	1.86	278	0.12	0.03
II@Al-BEN	1.85	269	0.11	0.04
Al-TERG	1.80	300	0.11	0.09
I@Al-TERG	1.78	210	0.06	0.12
II@Al-TERG	1.73	130	0.03	0.11

a consequence of the use of Tergitol in the preparation, which is in line with previous results [17].

The amounts of manganese determined by AAS encapsulated into the various materials after the in situ synthesis of the manganese(III) *salen* complexes **I** and **II** (Fig. 1) are collected in Table 2. It can be seen that the Mn contents lie between 28 and 42 μmol g^{-1}, which correspond to a complex encapsulation efficiency of 15–26% of the initial solution complex content; these values are lower than those obtained for the non-chiral Mn complexes reported before [20–22], which is a consequence of the larger dimensions of the chiral complexes. The manganese contents within **I**@Al-WYO, **I**@Al-BEN and **II**@Al-BEN are slightly higher within for **I**@Al-TERG and **II**@Al-TERG materials.

Upon encapsulation of the complexes, the textural properties of the PILC materials (Table 1) also show a significant lowering of surface area value (A_{BET}): from 338 to 278 and 269 $\text{m}^2\ \text{g}^{-1}$ for **I** and **II**, for the free and immobilised Al-BEN, respectively; and for Al-TERG, from 300 to 210 and 130 $\text{m}^2\ \text{g}^{-1}$ for **I** and **II**, respectively, although the general isotherm profiles were mainly retained as exemplified in Fig. 2 for the Al-BEN materials.

This lowering of surface area is attributed to the presence of the complexes into the pore structure of the PILCs and/or partially plugging the pores. It can also be observed in Table 1 that among the two complexes, encapsulation of phenyl substituted complex **II** (in both cases, Al-BEN and Al-TERG, but particularly for the latter) gives lowered surface areas, which may be attributed to the larger dimension of complex **II** compared to complex **I** [8b]. The microporous volume of the Al-BEN material is reduced to a lesser extent, after the encapsulation of complexes **I** and **II**, than what was observed for the Al-TERG material. In fact, for the latter solid the decrease in the microporous volume is about 45%, in the case of complex **I**, and 70% in the case of **II**. At first sight this result could seem somewhat contradictory. Actually, due to the use of Tergitol in the preparation of the Al-TERG material, micropores are expected to be wider in this solid than for Al-BEN, mainly due to the increase in the space between pillars. Nevertheless, it is difficult to have direct experimental evidence for these observations, since the precise characterisation of the distance between pillars is a difficult task. Furthermore, upon complex encapsulation the analysis of the pore size distribution in the mesopore region also shows some changes in the pore range between 2 and 4 nm: a shift towards smaller pore sizes is observed for both PILCs with encapsulated complex in comparison with the parent materials, indicating the presence of the complexes also in the mesopore structure.

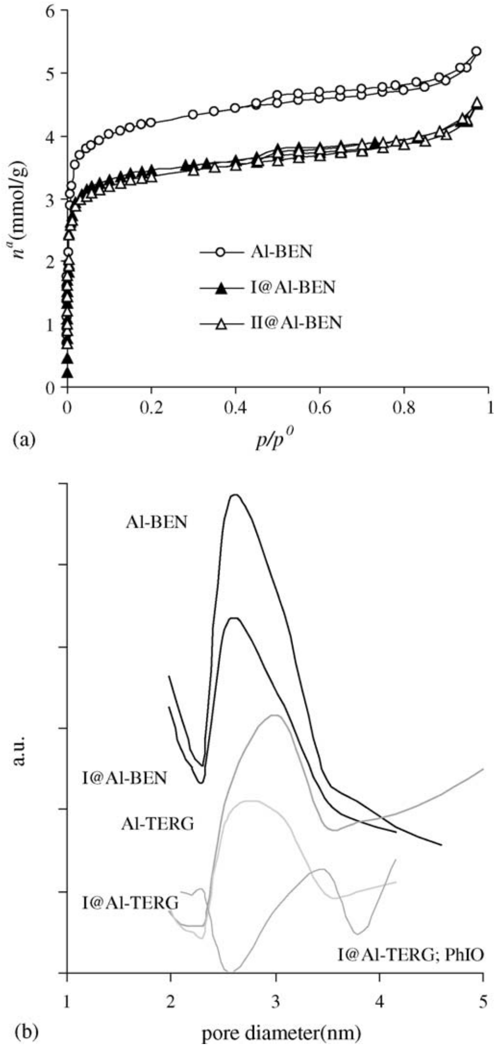

Fig. 2. (a) Typical adsorption–desorption nitrogen isotherms at −196 °C (b) and mesopore size distributions for the Al-BEN materials before and after encapsulation of the complexes **I** and **II**.

Table 2
Initial amounts (μmol) of the Mn(III) *salen* complexes per gram of PILC and amount of Mn determined by AAS and XPS

Sample	Mn (μmol g^{-1})			Encapsulation efficiency (%)[b]
	Initial	AAS	XPS[a]	
I@Al-WYO	170	41.7	76.9	24.5
I@Al-BEN	182	42.4	35.2	23.3
II@Al-BEN	160	41.7	26.1	26.1
I@Al-TERG	182	36.8	56.2	20.2
II@Al-TERG		27.8	20.4	15.3

[a] Mn amount per weight of sample (before catalytic tests) calculated from XPS data in this table: μmol Mn/weight of sample = at.% Mn/[at% C × Ar(C) + at.% N × Ar(N) + at.% O × Ar(O) + at.% Mg × Ar(Mg) + at.% Si × Ar(Si) + at.% Al × Ar(Al) + at.% Cl × Ar(Cl) + at.% Mn × Ar(Mn) + at.% Fe × Ar(Fe)].

[b] Encapsulation efficiency (%) = μmol Mn obtained by AAS × 100/initial μmol Mn.

However, it should be emphasised that, as discussed from the results in Table 1, and as is clearly noticed from the isotherms for Al-BEN before and after encapsulation, Fig. 2a—it is mainly the microporosity that is affected and, therefore, this is the part of the solid were most probably the complexes will be preferentially located. Mesopore size distributions were obtained from the nitrogen adsorption isotherms by the Broekhoff-de Boer method [25], simplified with the Frenkel–Halsey–Hill equation [26], and the results, for selected samples, are given in Fig. 2b. It can be observed from this figure that for Al-BEN, the maximum and the shape of the distributions, are much unchanged before and after the encapsulation (complex **I** in the example), supporting the above considerations that complexes are most probably located in the microporosity. In the case of the Al-TERG samples, before and after encapsulation, we believe that the differences found in the distributions are also minimal. Therefore, these differences are unlikely to justify a different conclusion for Al-TERG, as already stated for Al-BEN, that is, the complexes are also most probably located in the microporosity, in line with decrease in the microporous volumes in Table 1. The slight increase in the mesoporous volumes that is depicted in Table 1 for the Al-TERG samples after encapsulation can be a consequence of different arrangements of the secondary pores, that is, the contribution to the porosity (essentially to the mesoporosity) that comes from the arrangements of the clay particles. For certain clays, this type of porosity can result in significant values of mesoporous volumes [27].

The elemental composition of the materials by XPS show changes after encapsulation of the manganese(III) *salen* complexes (Table 3): an increase in the nitrogen and manganese content, confirming the presence of the manganese(III) *salen* complexes in the aluminium pillared clays. Nevertheless, for all materials compared with the parent ones, a decrease in the aluminium content is observed, as well as of the Al/Si ratio, suggesting the presence of host/guest interactions between the manganese(III) *salen* complexes and the PILCs matrix and/or changes in the composition/structure of the PILCs after the complex encapsulation process, as has been observed by us in the encapsulation of the achiral manganese(III) *salen* complex into the Al-WYO PILC [20–22].

The infrared spectra of all PILCs with encapsulated chiral complex show little differences compared to the spectra of the parent materials due to the combination of the low complex loading with the very strong clay absorptions. The IR spectrum of all PILCs show the intense and large bands due to the clay OH stretch in the region 3700–3300 cm^{-1}, those assigned to the surface hydroxyl groups from the acidic Al–OH group at 1630 cm^{-1} and finally in the range 1300–400 cm^{-1}, due to lattice vibrations (asymmetric stretching vibrations of SiO_2 tetrahedra) [28]. The very low intense bands due to complex vibrations are only observed between 1600 and 1300 cm^{-1}, which are due to N–H and C–H bending vibrations of the Schiff base ligand. Nevertheless, these observations indicate the presence of the manganese(III) *salen* complexes within the PILC galleries.

Similarly, the diffuse reflectance spectra of all PILCs with encapsulated chiral complex show little differences compared to the spectra of the parent materials (which absorb between 200 and 800 nm), also due to the combination of low complex loading within the materials and low intensity of the *d–d* bands of the manganese(III) *salen* complexes, preventing any information about the geometry of the encapsulated complexes.

3.2. Catalytic activity

The catalytic activity of the encapsulated Mn(III) *salen* complexes into the pillared clay materials was screened in the epoxidation of styrene at 0 °C using two different oxidants, PhIO and *m*-CPBA/NMO, and the results are summarised in Table 4 and Fig. 3.

The results show that all the pillared clay based materials are catalytically active in the epoxidation of styrene, showing moderate styrene conversion (up to 40%, entry 5). However, the enantiomeric excess (ee%) obtained by using these catalysts is very poor. Except for **I**@Al-TERG using with PhIO as oxidant (entry 16) for which 14 ee% was obtained, a value that is higher than the homogeneous phase reaction run under comparable conditions (entry 1), other systems showed either insignificant asymmetric induction or no ee%. In this exceptional case some synergetic effects on the *Jacobsen* complex (**I**) must occur within the micropore structure of the Al-TERG (see above characterisation section), whereas the other results point to large steric hindrances of both chiral Mn(III) *salen* complexes **I** and **II** within the PILCs porous structure during the course of the epoxidation of styrene, which result in very low or none asymmetric inductions on styrene epoxide. It is surpris-

Table 3
Areas under the XPS C 1s, O 1s, N 1s, Mg 1s, Al 2p, Si 2p, Cu $2p_{3/2}$ and Fe $2p_{3/2}$ bands (at.%) for the PILC materials

Sample	C	O	N	Mg	Al	Si	Mn	Cl	Fe	Al/Si	Mn/Si	Mn/Al
Al-WYO	8.32[a]	56.55	0.44	[b]	18.84	15.86			[b]	1.19		
I@Al-WYO	10.29	53.20	0.93	1.15	15.65	18.02	0.15	0.17	[b]	0.87	0.008	0.010
Al-BEN	9.99[a]	54.40	0.44	1.26	19.94	13.03		0.27	0.66	1.53		
I@Al-BEN	8.88	55.10	0.62	1.35	18.76	14.00	0.07	0.50	0.72	1.34	0.005	0.004
II@Al-BEN	15.55	51.84	0.90	1.46	16.09	12.82	0.05	0.61	0.69	1.26	0.004	0.003
Al-TERG	8.11[a]	56.46	0.17	1.19	16.01	16.59			0.84	0.97		
I@Al-TERG	12.35	52.77	1.04	1.32	14.99	16.40	0.11	0.24	0.78	0.91	0.007	0.007
II@Al-TERG	10.60	55.73	0.68	1.49	14.42	15.85	0.04	0.16	1.01	0.91	0.003	0.003

[a] Resulting from some hydrocarbon impurities adsorbed on the surface of the materials.

[b] Not determined.

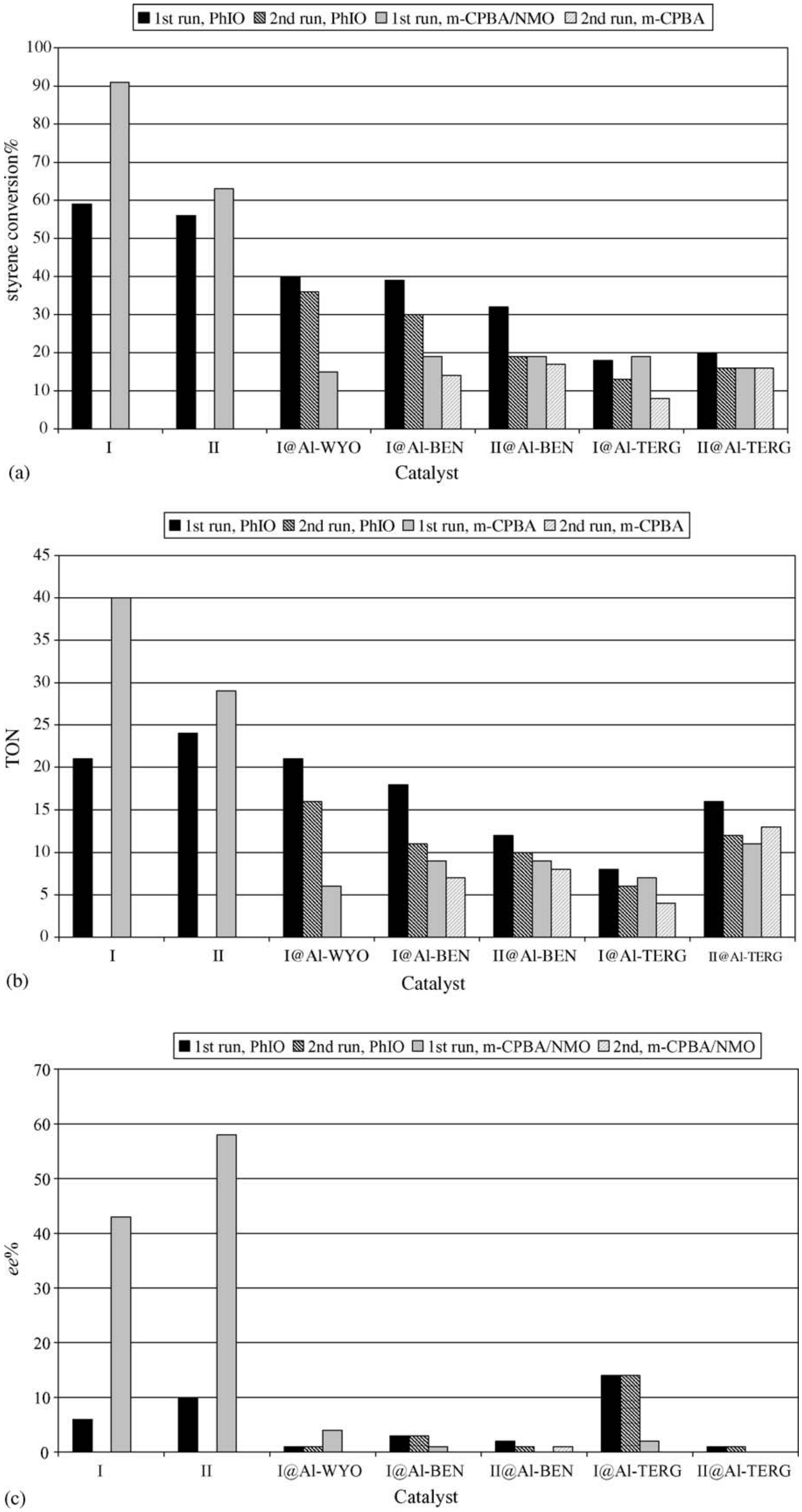

Fig. 3. Epoxidation of styrene catalysed by the Mn(III) *salen* complexes **I** and **II** in homogeneous phase and encapsulated in the PILCs Al-WYO, Al-BEN and Al-TERG using PhIO or *m*-CPBA/NMO as oxygen source: (a) styrene conversion %, (b) TON and (c) ee%.

ing to note that in homogenous phase using the oxidant system *m*-CPBA/NMO higher asymmetric induction are obtained with both Mn(III) *salen* complexes **I** and **II** than using PhIO, but with the encapsulated Mn(III) *salen* complexes into the PILCs insignificant asymmetric induction or no ee% was observed with this oxidant.

It can also be observed from Table 4 and Fig. 3 that under the same experimental conditions, but using PhIO as oxidant, the Al-WYO and Al-BEN based materials (entries 5–14) show higher styrene conversion compared to the Al-TERG based materials (entries 9 and 13), not only probably due to slightly higher Mn content, but probably also due to differences in the porosity, although the relation is not straightforward, since using *m*-CPBA/NMO as oxidant, comparable conversion are obtained for all the materials.

It is noteworthy that in all the cases the major product obtained was styrene epoxide along with benzaldehyde and small amount of unknown side product.

After the catalytic reaction the catalyst was separated, washed and re-used for a second time; with the exception of the catalyst **II**@Al-TERG with the oxidant *m*-CPBA/NMO (entry 23), the conversions decrease either marginally (entries 9, 11, 15 and 21) or slightly (entries 13, 17 and 19), though ee% remains unaffected (entries 9 and 17). The general decrease in catalytic activity of the catalyst after reuse is higher for the *m*-CPBA/NMO oxidant system than for PhIO, and has been attributed in the literature to degradation of the ligand under the strong oxidant *m*-CPBA/NMO [3c,5f,9]. Moreover, other effects can be used to explain these results: (i) leaching of metal complexes from the materials or (ii) blocking of the pores either by inactive Mn(IV)-oxo species believed to be generated during the catalytic mechanism [9] or by some other insoluble degraded product obtained by side reactions, which after several washing could not be removed from the materials or (iii) collapsing of some of the pillars during the catalysis experiments.

The absence of Mn in the composition analysis of the filtrate after catalyst removal from reaction media combined with the absence of any conversion after addition of a fresh amount of oxidant to the filtrate indicate that the observed decrease in activity upon reuse of the catalyst is not due to metal complex leaching. Moreover, the comparison of the Mn content of the catalysts by AAS before and after catalysis (Table 5) indicates that there is a marginal decrease in this value after the catalytic reaction for Al-WYO and Al-BEN PILCs, but a surprising increase in Al-TERG complexes. The increase in Mn content in the latter materials may be due to collapsing of some of the pillars during catalytic process, which make the mass of the sample to decrease and thus indirectly increase the manganese content. Some confirmation for this can be gathered from temperature

Table 4
Asymmetric epoxidation of styrene catalysed by the homogeneous and heterogenised manganese(III) *salen* complexes **I** and **II**[a]

Entry	Catalyst[a]	Oxidant	Run	*t* (h)	*C* (%)[b]	ee%[c]	TON[d]	TOF[e] (h^{-1})
1	**I**	PhIO[f]		24	59[g]	6	21	1
2		*m*-CPBA/NMO[h]		3	91	43	40	13
3	**II**	PhIO[f]		24	56[g]	10	24	1
4		*m*-CPBA/NMO[h]		4	63	58	29	7
5	**I**@Al-WYO	PhIO[f]	First	24	40[g]	1	21	0.9
6			Second	24	36[g]	1	16	0.6
7		*m*-CPBA/NMO[h]	First	4	15	4	6	2
8	**I**@Al-BEN	PhIO[f]	First	24	39[g]	3	18	0.7
9			Second	24	30[g]	3	11	0.5
10		*m*-CPBA/NMO[h]	First	4	19	1	9	2
11			Second	4	14	0	7	2
12	**II**@Al-BEN	PhIO[f]	First	24	32[g]	2	12	0.5
13			Second	24	19[g]	1	10	0.4
14		*m*-CPBA/NMO[h]	First	4	19	0	9	2
15			Second	4	17	1	8	2
16	**I**@Al-TERG	PhIO[f]	First	24	18[g]	14	8	0.3
17			Second	24	13[g]	14	6	0.2
18		*m*-CPBA/NMO[h]	First	4	19	2	7	2
19			Second	4	8	0	4	1
20	**II**@Al-TERG	PhIO[f]	First	24	20[g]	1	16	0.6
21			Second	24	16[g]	1	12	0.5
22		*m*-CPBA/NMO[h]	First	4	16	0	11	3
23			Second	4	16	0	13	3

[a] Reactions were carried out with 0.1 g of heterogeneous catalyst.
[b] Determined by GC-FID against internal standard (chlorobenzene).
[c] Determined by chiral GC-FID.
[d] TON = moles of converted styrene/moles of manganese.
[e] TOF = TON/time of reaction.
[f] In acetonitrile; molar ratio styrene: PhIO = 2:1.
[g] Styrene conversion corrected for the limiting reagent: PhIO.
[h] In dichloromethane; styrene: *m*-CPBA:NMO = 1:2:5.

Table 5
Comparison of the characterisation of the PILCs with encapsulated complexes before and after catalysis

Catalyst	Oxidant	Mn (μmol g^{-1})		d_{001} (nm)		A_{BET} ($m^2 g^{-1}$)		V_{micro} ($cm^3 g^{-1}$)		V_{meso} ($cm^3 g^{-1}$)	
		Before	After	Before	After	Before	After	Before	After	Before	After
I@Al-WYO	*m*-CPBA/NMO	41.7	36.0	1.81	[a]	149	[a]	0.05	[a]	0.06	[a]
I@Al-BEN	PhIO	42.4	40.3	1.86	1.82	278	195	0.12	0.08	0.16	0.03
	m-CPBA/NMO	42.4	39.1	1.86	1.82	278	156	0.12	0.07	0.16	0.04
II@Al-BEN	PhIO	41.7	39.8	1.85	1.81	269	207	0.11	0.08	0.16	0.05
I@Al-TERG	PhIO	36.8	38.3	1.78	1.68	210	57	0.06	0.007	0.18	0.09
	m-CPBA/NMO	36.8	39.1	1.78	1.64	210	29	0.06	0.003	0.18	0.06
II@Al-TERG	PhIO	27.8	39.8	1.73	1.65	130	42	0.03	0.002	0.14	0.08
	m-CPBA/NMO	27.8	38.3	1.73	1.63	130	21	0.03	0.000	0.14	0.04

[a] Not determined.

nitrogen adsorption isotherms and X-ray diffractograms data colleted after the catalytic reaction.

In fact, the low temperature nitrogen adsorption isotherms before and after catalysis, illustrated in Fig. 4 for the Al-TERG samples, show significant changes: the specific surface area and porous volumes all decrease considerably after catalytic reaction, particularly the microporous volumes, as is clearly noticed by the changes in the initial part of the isotherms (Fig. 4). These observations are indicative of a partial collapse of the structure of the pillared clays which also has the consequence of shifting the mesopore size distributions to higher values, as exemplified in Fig. 2b) for the Al-TERG sample after encapsulation and catalysis with the PhIO oxidant.

Similarly, the d_{001} values of the Al-BEN materials after catalysis (Table 5) decreases about 0.04 nm and about 0.10 nm for Al-TERG materials, although the definition of the diffraction peaks (d_{001}) is, still, quite evident as can be noted in Fig. 5, where the X-ray diffractograms are presented for the Al-TERG samples before and after the catalytic experiments.

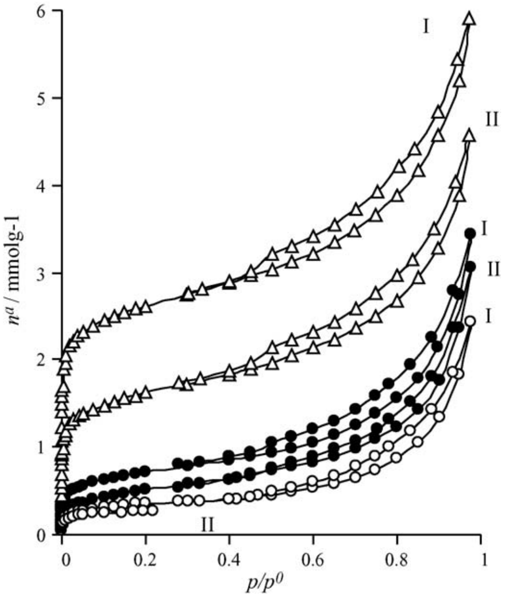

Fig. 4. Typical nitrogen adsorption–desorption isotherms at −196 °C of the Al-TERG samples with the complexes **I** and **II** before (triangles) and after (circles) the catalytic experiments. In the latter curves, open and closed symbols are for CPBA/NMO and PhIO oxidants, respectively.

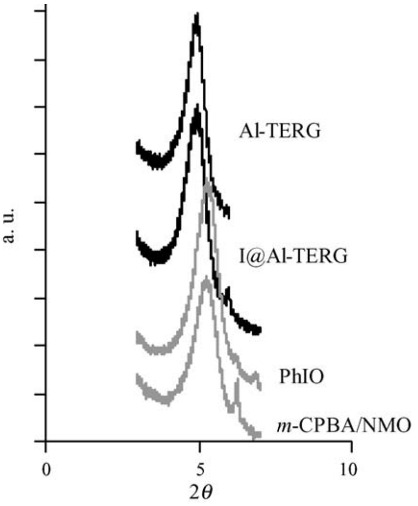

Fig. 5. Typical X-ray diffractograms for the Al-TERG materials. The curves for the samples after catalysis are identified by the respective oxidant.

4. Conclusions

Two chiral manganese(III) *salen* complexes, (*R,R*)-[Mn(3,5-dtButsalhd)Cl] (**I**) and (*R,R*)-[Mn(3,5-dtButsaldPh)Cl] (**II**) were encapsulated by in situ generation of the complexes inside pillared clays with different structural properties: two types of Al-PILCs derived from the same original clay Benavila (Al-BEN and Al-TERG). The chiral manganese(III) *salen* complex **I** was also encapsulated into an Al-pillared clay (Al-WYO) derived from the another original clay (Wyoming).

Slightly higher quantities of both chiral manganese(III) *salen* complexes were encapsulated into the PILCs Al-WYO and Al-BEN than into the PILC, Al-TERG. The main differences in the preparation of these PILCs comes from the fact that the latter was prepared by a methodology that involved the use of a polyalcohol as a surfactant to act as an interlayer gallery template.

The encapsulated complexes also cause a significant decrease in the initial surface area value (A_{BET}) and the microporous volumes of the non-encapsulated PILCs. These observations and the analysis of the mesopore size distributions, lead us into the conclusion that the encapsulation of the complexes mainly occurs in the micropores.

The chiral manganese Al-pillared clay based materials acted has active heterogeneous catalysts in the epoxidation of styrene using PhIO or *m*-CPBA/NMO as oxidants, with moderate alkene conversions (16–40%), but generally very poor asymmetric inductions were obtained (0–14%). Nevertheless, for **I**@Al-TERG using with PhIO as oxidant 14 ee% was obtained, which is higher than the homogeneous phase reaction run under comparable conditions, probably due to synergetic effects on the *Jacobsen* complex (**I**) within the micropore structure of the Al-TERG. To our knowledge, and regarding the ee%, this is the most favourable result in the literature when using manganese(III) *salen* complexes supported in pillared clays. The low asymmetric induction exhibited by the other catalysts point to large steric hinderances of both chiral Mn(III) *salen* complexes **I** and **II** within the other PILCs porous structure during the course of the epoxidation of styrene. In line with these latter conclusions we intend, in future works, to use clay based materials with more open porosity.

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