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Epoxidation of styrene by a manganese(III) salen complex encapsulated in an aluminium pillared clay

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The manganese(III) complex—carboxylate-[*N*,*N*′-bis(salicylaldehyde)cyclohexanediaminate]manganese(III), [Mn(salhd)CH_3COO]—was encapsulated into an aluminium pillared clay (denoted as Al-WYO) using a two-step liquid phase methodology: (i) adsorption of manganese(II) acetate in ethanolic solution within Al-WYO, followed by (ii) diffusion of *N*,*N*′-bis(salicylaldehyde)cyclohexanediamine in ethanolic solution. The new material was characterised by several techniques (ICP-AES, XPS, FTIR, UV–Vis and low temperature nitrogen adsorption) which showed that *in situ* synthesis of the manganese(III) complex took place within the aluminium pillared clay porous structure.

The catalytic activity of the heterogenised [Mn(salhd)CH_3COO] in the epoxidation of styrene was studied in acetonitrile, at room temperature, using iodosylbenzene or sodium hypochlorite as oxygen source. With PhIO the new heterogeneous catalyst showed high styrene epoxide chemoselectivity and could be reused at least 3 times without significant loss in styrene epoxide yield, suggesting that no complex leaching took place under the reaction conditions used. When sodium hypochlorite was used as oxidant, high selectivity in by-products was observed, as well as extensive leaching of the catalyst into solution. XPS spectra of the catalyst after the catalytic reaction confirm manganese complex leaching and also show a significant decrease in aluminium content, thus suggesting that partial damage of aluminium pillars took place in this reaction media, inducing complex leaching.

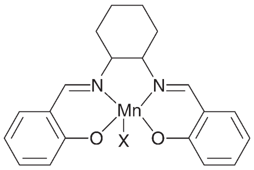
Introduction

Transition metal complexes with Schiff base ligands have been extensively used in homogeneous catalysis, mainly because of their high activity, selectivity and enantioselectivity (when chiral complexes are used).[1] Namely, manganese(III) *salen* complexes have been reported as efficient catalysts for the epoxidation of unfunctionalised alkenes in homogeneous phase,[2,3] with a wide range of oxidants—for example, iodosylbenzene, sodium hypochlorite and hydrogen peroxide.[4] Recently, the heterogenisation of these homogeneous catalysts in porous solids has been the subject of intense research in order to make the system recyclable and more stable.[1,5,6] Several supports have been used, such as zeolites, clays, other porous-structured materials[5] and more recently, activated carbons.[6,7]

Pillared clays (PILCs) are a newly developed family of porous materials obtained by exchanging the interlayered cations of swelling clays with bulky inorganic polyoxo and polyoxy cations. Upon calcination they are converted into metal oxide clusters creating an interlayer space of molecular dimensions and a well defined pore system. The catalytic properties of PILCs are mainly related to their acid character,[8,9] and have been used in hydrogenation, hydrotreating and isomerisation reactions. The incorporation of transition metals into the composition of Al-PILCs not only increases their Brønsted acidity, but also allows their use in catalytic redox reactions.[9,10]

We have been interested in the heterogenisation of transition metal complexes with catalytic activity in zeolites,[11,12] activated carbons[6,7,13–15] and aluminium pillared clays,[16–18] and we have shown that the methodologies used for immobilisation of metal complexes are largely determined by the supports. We have successfully entrapped Schiff base nickel(II) and copper(II) complexes by the *in situ* method within the porous of zeolites[11,12] and aluminium pillared clays[16,18] and by the simultaneous aluminium oxide pillaring/encapsulation of Schiff base copper(II) complexes into a montmorillonite;[17] these complexes have acted as probe molecules for the development of the different methods for metal complex immobilisation within the pillared clays.

Herein, we report the encapsulation and characterisation of a non-chiral manganese(III) salen complex, [Mn(salhd)CH_3-COO] (Scheme 1) into an aluminium pillared clay and its catalytic activity in the epoxidation of styrene in acetonitrile, at room temperature, either using iodosylbenzene (PhIO) or sodium hypochlorite (NaOCl) as the oxygen sources. The Al-PILC used, denoted as Al-WYO, was characterised in a previous work. [19] The manganese(III) complex was encapsulated



Scheme 1 Molecular structure of [Mn(salhd)X] (X = CH_3COO).

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in the pores of Al-WYO by ligand diffusion in a previously Mn(II) modified aluminium pillared clay. Characterisation of the new material, [Mn(salhd)CH_3COO]@Al-WYO, by chemical analysis, XPS and spectroscopic techniques (FTIR and UV–vis) showed that the Mn(III) complex has been efficiently immobilised within the Al-WYO porous structure; furthermore, [Mn(salhd)CH_3COO]@Al-WYO showed, in acetonitrile, high epoxide chemoselectivity in the heterogeneous epoxidation of styrene using PhIO as the oxygen source.

Experimental

Solvents and reagents

The reagents and solvents used in the synthesis of the Schiff base complex, in the modification of the aluminium pillared clay and in the catalytic experiments were used as received, except for 1,2-diaminocyclohexane which was purified by distillation. Salicylaldehyde, 1,2-diaminocyclohexane, manganese(II) acetate tetrahydrate, styrene, chlorobenzene, benzaldehyde, styrene epoxide and sodium hypochlorite solution were from Aldrich. All the solvents were from Merck (*pro analysi*), except acetonitrile and dichloromethane used in the catalytic experiments, which were from Romil (HPLC grade). Iodosylbenzene was synthesised according to procedures described in the literature.[20]

Parent material

The pillared clay (Al-WYO) was prepared as described detailed elsewhere.[19] Briefly, a montmorillonite from Wyoming (USA) was used as starting material, whose structural formula, based on chemical analysis and cation exchange capacity data, is: $(Si_{3.91}Al_{0.09})^{IV}(Al_{1.51}Fe_{0.18}Mg_{0.26})^{VI}(Ca_{/2}, K, Na)_{0.49}$. The clay was pillared with an oligomer solution made from $AlCl_3$ and NaOH. After washing and freeze-drying the solid was calcined at 350 °C, for two hours after a ramp of 1 °C min^{-1}.

Preparation of complex and its heterogenisation

The synthesis and characterisation of the Schiff base ligand *N*,*N*′-bis(salicylaldehyde)cyclohexanediamine (H_2salhd) and corresponding complex chloro-[*N*,*N*′-bis(salicylaldehyde)-cyclohexanediaminate] manganese(III), ([Mn(salhd)Cl]), has been reported by us elsewhere.[3,6]

The manganese complex was immobilised within the Al-WYO by the *in situ* synthesis of the complex, using a two-step liquid phase methodology: (i) to 1.0 g of previously dried Al-WYO were added 0.12 g (0.50 mmol) of manganese(II) acetate tetrahydrate dissolved in a mixture of methanol (10 cm^3)–ethanol (40 cm^3), and the resulting suspension was refluxed for 3 hours, (ii) then 0.16 g (0.50 mmol) of H_2salhd dissolved in ethanol were added to the suspension, and the mixture was further refluxed for 3 hours. The new material, [Mn(salhd)CH_3COO]@Al-WYO, was sequentially purified by Soxhlet extraction with 150 cm^3 of ethanol, dichloromethane and acetonitrile in order to remove residual reactants or complexes physically adsorbed on the external surface of the material. Finally, it was dried in an oven at 120 °C for 12 hours, under vacuum.

Physico-chemical measurements

The elemental chemical analyses (Si, Al, and Mn) were performed by Kingston Analytical Services (UK), using inductively coupled plasma atomic emission spectroscopy (ICP-AES). X-Ray photoelectron spectroscopy was performed at "Centro de Materiais da Universidade do Porto" (Portugal), in a VG Scientific ESCALAB 200A spectrometer using a non-monochromatised MgKα radiation (1253.6 eV). All the materials were compressed into pellets prior to the XPS studies. In order to correct possible deviations caused by electric change of the samples, the C 1s line at 285.0 eV was taken as internal standard.[21,22]

Nitrogen adsorption isotherms at −196 °C of parent and modified materials were determined in a Micromirectics Asap 2010 apparatus; before the measurements the samples were outgassed (under vacuum) overnight at 50 °C.

FTIR spectra were obtained as potassium bromide pellets in the range 400–4000 cm^{-1} with a Jasco FT/IR-460 Plus spectrophotometer. Diffuse reflectance UV–vis spectra were registered on a Shimadzu UV/3101PC spectrophotometer in the range 1500–200 nm.

GC-FID chromatograms were obtained with a Varian CP-3380 gas chromatograph using helium as carrier gas and a fused silica Varian Chrompack capillary column CP-Sil 8 CB Low Bleed/MS (30 m × 0.25 mm id; 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.

Catalytic experiments

The catalytic activity of the new material in the epoxidation of styrene was assessed at room temperature. In the experiments using PhIO as oxidant in acetonitrile, 0.500 mmol of styrene (substrate), 0.500 mmol of chlorobenzene (GC internal standard), 0.100 g of heterogeneous catalyst and 0.250 mmol PhIO were added, under stirring, to 5.00 cm^3 of acetonitrile. During the experiment 0.1 cm^3 aliquots were taken from solution, with a hypodermic syringe, filtered through 0.2 μm syringe filters and directly analysed by GC-FID. After the time needed for total consumption of PhIO (the ratio of areas of iodobenzene and chlorobenzene in chromatogram was constant), the solution was separated by centrifugation and removed to a new flask. To ensure that the epoxidation was only catalysed heterogeneously, PhIO (0.25 mmol) was added to the separated solution and the composition of reaction media was monitored. After utilisation, the catalyst was washed/centrifuged with methanol (five times) and then with acetonitrile (two times) to remove occluded reactants and products, dried and was then reused using the same experimental conditions described above. The cycle catalysis–washing was performed three times. To assess the eventual catalytic activity of the support in the epoxidation of styrene, reactions using the same experimental conditions (*vide supra*) were also carried out in the presence of the support (0.1 g); negligible activity for the support was found using PhIO as oxidant.

In the experiments with NaOCl aqueous solution as oxygen source, in acetonitrile or dichloromethane, 1.000 mmol of styrene (substrate), 1.500 mmol of chlorobenzene (GC internal standard), 0.100 g of catalyst and 0.25 cm^3 of NaOCl (4.00 mmol) were added, under stirring, to 5.00 cm^3 of acetonitrile or dichloromethane. The solution was buffered to pH ≈ 11 (1.5 cm^3 of $NaH_2PO_4 + NaHO$), to minimise formation of chlorinated products.[3,23] The same experimental procedure was used as described above for the experiments with PhIO. To ensure that the epoxidation was only catalysed heterogeneously, a new portion of the reactant needed was added to the separated solution and the composition of reaction media was monitored. After utilisation, the catalyst was washed with methanol (five times) and then with acetonitrile (two times), to remove occluded reactants and products, dried and compressed into a pellet to be analysed by XPS.

Identification and quantification of products were made by GC-FID analysis (internal standard method). The assignation was made by comparison with authentic samples; retention times (in the experimental conditions used): chlorobenzene 6.4, styrene 7.5, benzaldehyde 9.7, iodobenzene 12.3 and styrene epoxide 13.1 min.

Results and discussion

Characterisation of the material

The elemental analysis and the surface atomic contents of Al-WYO and [Mn(salhd)CH_3COO]@Al-WYO, obtained by ICP-AES and XPS, are presented in Table 1.

The manganese contents of the encapsulated complex obtained from XPS (surface analysis) and ICP-AES (bulk analysis) are similar, indicating that Mn complex is homogeneously distributed throughout the pillared clay. The modified clay, [Mn(salhd)CH_3COO]@Al-WYO, contains 0.197 mmol of complex per gram of aluminium pillared clay, indicating that only some of the loaded manganese(II) acetate has been coordinated to H_2salhd and entrapped in the Al-WYO (*vide* experimental), leading to a complex encapsulation efficiency of 40%; this value is the highest transition metal complex loading obtained using an aluminium pillared clay, notwithstanding that different immobilisation procedures have been used in the previous studies reported by us.[16–18]

Upon complex encapsulation there is an increase in silicon content and a decrease in the aluminium content, in both surface and bulk quantities, leading to a decrease in the Al/Si ratio; these results suggest that some composition/structural changes took place upon complex immobilisation.

The high resolution XPS spectra for Al-WYO pillared clay are very similar to those already reported by us for pillared clays based on natural Portuguese smectites.[17,18] The Si 2p high resolution XPS spectra of the Al-WYO and [Mn(salhd)-CH_3COO]@Al-WYO show bands at about 103 eV with a low lying energy shoulder at about 100 eV, which correspond, respectively, to silicon from the tetrahedral sheets of the clay and to silicon with a different chemical environment, such as terminal Si–OH groups[24] and/or Si–O–Al groups formed between the tetrahedral silicon and the pillaring oligomers after calcination. In the Al 2p region, a symmetrical band centred at 75 eV due to the aluminium from the clay lattice and from the alumina pillars is observed. The [Mn(salhd)CH_3-COO]@Al-WYO also shows in the Mn 2p region a very large band due to the presence of the Mn centre: the broad Mn $2p_{3/2}$ bands have maxima at about 642 eV, in agreement with the values reported for manganese(III) complexes with salen[25] and porphyrinic[26] ligands.

The textural properties of the samples, evaluated from the low temperature nitrogen adsorption (Fig. 1) revealed a decrease of the specific surface area (A_{BET}) from 196 $m^2\ g^{-1}$ in the Al-WYO to 106 $m^2\ g^{-1}$ in the sample with the complex. The microporous volumes (estimated from the *t*-method[27]) also decreased from 0.07 to 0.03 $cm^3 g^{-1}$, on going from the parent material to that with the complex. These results, combined with the observation that the curves are much similar in the region of the adsorption in mesopores ($p/p^0 > 0.4$), suggests that encapsulation of [Mn(salhd)CH_3COO] took place, and mostly in the microporosity of the Al-WYO.

The FTIR spectra of Al-WYO, [Mn(salhd)CH_3COO]@Al-WYO and [Mn(salhd)Cl] are presented in Fig. 2. Similarly to the aluminium pillared clays based on natural Portuguese smectites (Al-BEN) reported elsewhere,[17] the spectrum of Al-WYO shows typical intense and large bands in the region 3700–3300 cm^{-1}, which are assigned to the surface hydroxyl groups from the acidic Al–OH group;[28–30] at 1630 cm^{-1} due to physisorbed water and in the range 1300–400 cm^{-1}, from lattice vibrations[17,28] (asymmetric stretching vibrations of SiO_2 tetrahedra).[29] In addition to these strong bands due to the parent material, the [Mn(salhd)CH_3COO]@Al-WYO spectrum also shows low intense bands in the 1600–1200 cm^{-1} region, where the Al-WYO matrix does not absorb (Figs. 2a and 2b), which are assigned to the manganese(III) salen complex.

The bands due to the encapsulated manganese(III) salen complex are broader and their frequency and intensity are slightly different from those of free complex (Figs. 2b), suggesting that the manganese(III) salen complex might be distorted as a consequence of the physical constraints imposed by the matrix and/or has some host–guest interactions with PILC structure, as observed for copper(II) complexes entrapped in Al-BEN.[16–18]

The diffuse reflectance UV–vis spectrum of [Mn(salhd)CH_3-COO]@Al-WYO is very similar to that of the parent material (Al-WYO). The non-observance of characteristic complex bands is a consequence of several combined factors: (i) small extinction coefficients of manganese(III) complex electronic bands, (ii) low manganese(III) salen content within the aluminium pillared clay and (iii) background absorption of parent material in the near ultraviolet–visible region. Accordingly, no electronic/structural information on the entrapped manganese(III) salen complex could be gathered by this technique.

Catalysis experiments

In the catalytic epoxidation of alkenes the choice of oxygen donor and solvent is of crucial importance. In this study we chose two of the most used oxidants in epoxidation reactions, PhIO and NaOCl, and acetonitrile as reaction media.[1–5] Because sodium hypochlorite solution is partially miscible with acetonitrile, leading to extensive hydrolysis of the styrene epoxide,[3] dichloromethane was also tested as reaction media with this oxidant. The results of epoxidation of styrene, at room temperature, catalysed by the homogeneous and heterogeneous Mn(III) salen catalysts are summarised in Table 2.

The [Mn(salhd)CH_3COO]@Al-WYO heterogeneous catalyst shows high styrene epoxide chemoselectivity (Table 2 and Fig. 3) using PhIO as oxygen source in acetonitrile. Moreover, no catalytic activity in the epoxidation of styrene was observed in the filtrate after catalyst filtration, suggesting that the reaction was only catalysed heterogeneously and that no leaching of the active phase to solution took place.

The percentage of styrene conversion, as well as the styrene epoxide selectivity (and therefore, styrene epoxide yield), are constant after catalyst reuse twice (Table 2 and Fig. 3). However, a slight decrease of these parameters was observed on the fourth cycle of catalyst utilisation (Table 2 and Fig. 3); this result can not be attributed to manganese(III) salen complex leaching, since no catalytic activity was found in the solution after catalyst removal. It is possible that during the previous

Table 1 ICP-AES and XPS results for the parent aluminium pillared clay and with the complex encapsulated

	XPS[a] (atomic %)						ICP-AES/mmol g^{-1}				
Sample	Al	Si	Mn	Na	Al/Si	Mn/Si	Al	Si	Mn	Al/Si	Mn/Si
Al-WYO	18.84 (9.59)	15.86 (8.07)			1.19		6.26	5.38		1.16	
[Mn(salhd)ac]@Al-WYO	15.81 (8.14)	16.52 (8.51)	0.39 (0.20)	0.04	0.96	0.024	5.86	5.59	0.197	1.05	0.035
[Mn(salhd)ac]@Al-WYO[b]	8.73 (4.33)	10.27 (5.09)	0.17 (0.08)	14.38	0.83	0.016					

[a] Values between brackets refer to mmol g^{-1}, calculated as described elsewhere.[17] [b] After a catalytic reaction with NaOCl.

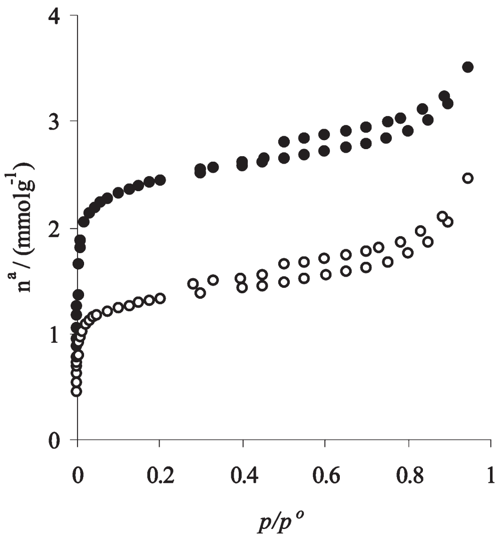

Fig. 1 Nitrogen adsorption isotherms at −196 °C: ● Al-WYO and ○ [Mn(salhd)CH_3COO]@Al-WYO.

reaction cycles, low extent deactivation of the active species took place, by formation of dimeric Mn(IV) salen species within the PILC, leading to a decrease in the catalyst activity. Hence, from data in Table 2 and Fig. 3 it is clear that the new heterogeneous catalyst does not significantly lose its efficiency (similar styrene conversion and styrene epoxide yield) after three catalytic cycles with iodosylbenzene as the oxygen source, suggesting that complex immobilisation by *in situ* synthesis within the pores of the aluminium pillared clay was effective; moreover, no structural changes of the Al-WYO took place under the experimental conditions used.

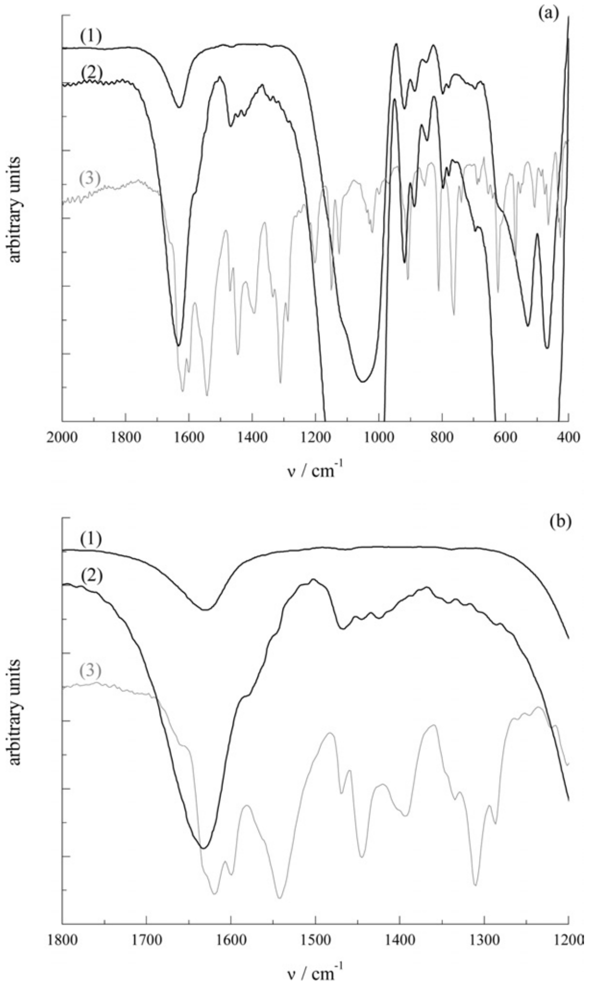

Fig. 2 FTIR spectra: (a) in the range 2000–400 cm^{-1} (1) Al-WYO, (2) [Mn(salhd)CH_3COO]@Al-WYO and (3) [Mn(salhd)CH_3COO]; (b) in the region 1800–1200 cm^{-1}: (1) Al-WYO, (2) [Mn(salhd)CH_3COO]@Al-WYO and (3) [Mn(salhd)CH_3COO].

The styrene epoxide selectivity is lower than that obtained in an experiment run in homogeneous phase, under comparable experimental conditions (Table 2), which may be attributed, not only to some low extent epoxide ring opening (Table 2) due to surface acidity of the support, but also to the distortions of the complex due to physical constraints imposed by the matrix and/or to host–guest interactions.

Physical entrapment of manganese(III) salen complexes in zeolites generally led to lower epoxide selectivities when compared to homogeneous phase reactions, under comparable experimental conditions.[5] Garcia *et al.*[1,5,31] encapsulated the chiral manganese(III) salen complex of Scheme 1 within the zeolite Y, and observed lower styrene epoxide selectivity (61%) than the homogeneous counterpart (80%), using NaOCl in dichloromethane at 5 °C. The manganese(III) salen complex in Scheme 1 encapsulated within Al-WYO, reported herein, gives rise to higher styrene epoxide selectivity (75%) than within the zeolite Y, notwithstanding the different experimental conditions used.[1,5,31] The Al-WYO possesses a more open structure with larger micropores than zeolites, minimising physical constraints imposed by the matrix. This permits the preservation of a microenvironment comparable to that of homogeneous phase, and consequently, allowing for a higher styrene epoxide selectivity. Reports on physical entrapment of manganese(III) salen complexes in zeolites[1,5,31] give no information on catalyst reuse, although the authors stated that no complex leaching took place during the epoxidation reaction.

Comparing the homogeneous and heterogeneous phase reactions, performed under comparable experimental conditions, it can also be observed that with the heterogeneous catalyst the reaction time increases and styrene conversion decreases (Table 2). The first is a general effect that arises upon immobilisation of metal complex catalyst in porous matrices and has been attributed to diffusional constraints imposed on substrates and reactants by the porous network of the matrix. The diffusion of the reactants to the metal centre can be particularly hindered for PhIO, a solid with low solubility in acetonitrile and that solubilisation is controlled by its rate of consumption.[32] The latter effect, lower styrene conversion, must be due to consumption of PhIO in competing reactions involving the matrix.[6,7]

When NaOCl is used as the oxygen source, either in acetonitrile or dichloromethane, the catalyst [Mn(salhd)CH_3COO]@Al-WYO originates low styrene epoxide chemoselectivity and large quantities of other by-products (Table 2). The catalytic reaction was also performed with Al-WYO using comparable experimental conditions and unpredictably similar activity in styrene conversion to that of metal complex based catalysts was observed in both solvents (Table 2): the activity is higher in acetonitrile (100% of styrene conversion in 24 h) than in dichloromethane, probably due to the complexity of the reaction in dichloromethane,[3] which consists of a three phase system resulting in enhanced diffusional limitations. Moreover, Al-WYO shows higher chemoselectivities for by-products than for styrene epoxide in both solvents, also as the metal based heterogeneous catalysts.

In these experimental conditions, high catalytic activity was observed in the filtrate after catalyst removal at the end of reaction, in opposition to what was observed with PhIO, which clearly indicates extensive leaching of the manganese(III) salen complex into the reaction media. These latter results, combined with the good catalytic activity of [Mn(salhd)CH_3COO]@Al-WYO using PhIO, suggest that significant changes might occur in the PILC structure during catalytic reaction when NaOCl is used.

Table 2 Epoxidation of styrene, at room temperature, catalysed by the homogeneous and heterogeneous [Mn(salhd)X]

					% Selectivity (% yield)[e]		
Catalyst	Oxidant	Cycle	t/h	% C[e]	Styrene epoxide	Benzaldehyde	Others[g]
[Mn(salhd)Cl][a]	PhIO		2[d]	71[f]	97 (69)	3 (2)	0 (0)
Al-WYO[a]	PhIO		48	1[f]	16 (0)	84 (1)	0 (0)
[Mn(salhd)ac]@Al-WYO[a]	PhIO	1st	48[d]	43[f]	75 (32)	20 (9)	5 (2)
	PhIO	2nd	48[d]	40[f]	74 (30)	21 (8)	5 (2)
	PhIO	3rd	48[d]	40[f]	74 (30)	22 (9)	5 (2)
	PhIO	4th	48[d]	34[f]	69 (23)	28 (9)	3 (1)
[Mn(salhd)Cl][b]	NaOCl		4	91	50 (45)	16 (15)	34 (31)
Al-WYO[b]	NaOCl		48	100	30 (30)	16 (16)	54 (54)
[Mn(salhd)ac]@Al-WYO[b, h]	NaOCl	1st	48	100	38 (38)	21 (21)	41 (41)
[Mn(salhd)Cl][c]	NaOCl		4	34	60 (20)	10 (4)	30 (10)
Al-WYO[c]	NaOCl		48	17	10 (2)	25 (4)	65 (11)
[Mn(salhd)ac]@Al-WYO[c, h]	NaOCl	1st	72	38	11 (4)	22 (8)	67 (26)

[a] In acetonitrile and molar ratio styrene/PhIO = 2:1. [b] In acetonitrile and molar ratio styrene/NaOCl = 1:4. [c] In dichloromethane and molar ratio styrene/NaOCl = 1:4. [d] Time needed for complete consumption of the oxidant. [e] Determined by GC-FID against internal standard (chlorobenzene). [f] Styrene conversion corrected for the limiting reactant (PhIO). [g] Others = other reaction products. [h] Leaching of the metal complex into solution was observed.

In order to assess eventual changes in Al-WYO structure induced by catalytic reaction conditions, XPS spectra of [Mn(salhd)CH$_3$COO]@Al-WYO were obtained after removal from the reaction media. Several changes in elemental surface composition were detected and the most significant were the decrease in manganese and aluminium contents and increase in sodium quantity (Table 1). Manganese content decrease undoubtedly confirms complex leaching suggested by the catalytic activity of the filtrate; dealumination might be a consequence of partial pillar hydration/decomposition induced by alkaline pH of the reaction media and increase in sodium quantity might result from ionic exchange of counter cations from the PILC with sodium from the oxidant. The straightforward conclusion here is that complex leaching is a consequence of the partial damage of the porous PILC structure.

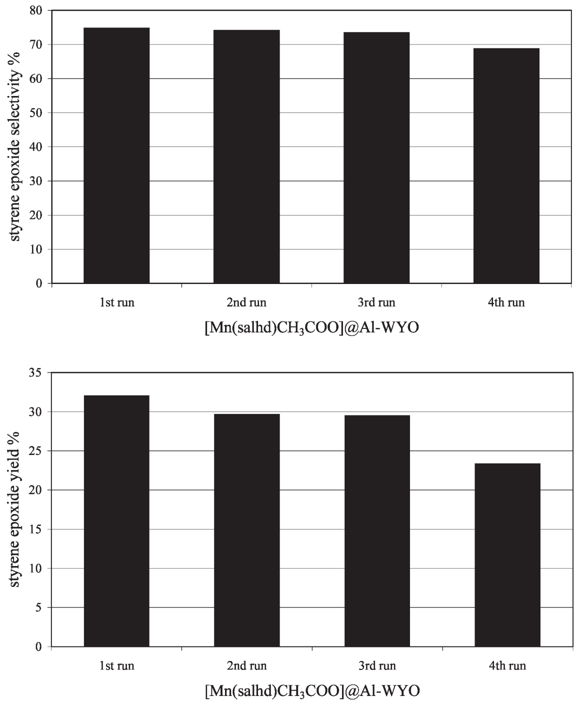

Fig. 3 Epoxidation of styrene catalysed by [Mn(salhd)CH$_3$COO]@Al-WYO with PhIO as oxygen source in acetonitrile: (a) styrene epoxide selectivity (%) and (b) styrene epoxide yield (%).

A comment must be made relating to the success of complex immobilisation within Al-WYO by the *in situ* method, as the results observed for the catalytic reaction using NaOCl would lead us to conclude the opposite. It must be emphasized that a successful complex immobilisation must involve not only the efficiency of the immobilisation strategy, but also the stability of the resulting material (support and complex) under the experimental catalytic reaction conditions.

Conclusions

A new heterogeneous catalyst has been prepared by salen ligand diffusion in Mn(II) modified Al-WYO (*in situ* synthesis method). The manganese(III) salen complex is mainly physically entrapped uniformly throughout the matrix and it is distorted due to physical constraints imposed by the matrix and/or owing to host–guest interactions.

The new material [Mn(salhd)CH$_3$COO]@Al-WYO has been tested in the catalytic epoxidation of styrene at room temperature. Using PhIO as oxygen source in acetonitrile, the new heterogeneous catalyst showed high styrene epoxide chemoselectivity and could be reused at least three times without significant loss in styrene epoxide yield. No leaching was also observed in between the catalytic reuses, confirming stability of the support under the experimental conditions used and an efficient complex immobilisation methodology.

Heterogeneous epoxidation of styrene with sodium hypochlorite as oxidant leads to extensive leaching of the molecular catalyst into solution, as well as high selectivity in by-products, either using acetonitrile or dichloromethane as reaction media. Catalyst XPS spectra after reaction showed a decrease in manganese and aluminium contents, suggesting that in this specific experimental conditions partial damage of aluminium pillars took place, inducing metal complex leaching.

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