Catalytic Properties of a Mn^{III}-Salen Complex Immobilised in a Pillared Clay by Simultaneous Pillaring/Encapsulation Procedures

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The simultaneous encapsulation of a manganese(III)-salen complex, [Mn(salhd)Cl], and pillaring of a montmorillonite clay with aluminium polyoxycations was performed using two methods: method A – the [Mn(salhd)Cl] complex was dissolved in ethanol and added to the oligomer solution at a stage when the oligomeric species had already formed; method B – the complex, also dissolved in ethanol, was added to the clay dispersion. After calcination, both materials were Soxhlet extracted to remove the excess complex, and characterised by XRD, nitrogen adsorption at –196 °C, XPS, atomic absorption and FTIR spectroscopy. In both cases, the manganese(III)-salen complex is mainly physically entrapped within the matrix, although some host–guest interactions with the matrix may be present. Both new materials [Mn(salhd)Cl]@Al-WYO_A and [Mn(salhd)Cl]@Al-WYO_B show catalytic activity in the epoxidation of styrene at room temperature with PhIO as oxygen source in acetonitrile. The solids present high styrene epoxide selectivity, and may be reused at least four times. FTIR spectra of the catalysts after the catalytic reactions suggest that during the reaction no structural changes of the pillared clay (PILC) took place, but low extent complex leaching occurred.

Introduction

Pillared clays (PILCs) are a relatively well-known class of materials, whose preparation methods and catalytic properties were reviewed by different authors.[1–3] Since PILCs were initially developed because of their potential as solids with larger pores than traditional zeolites, namely those used in cracking catalysis, a large number of studies were directed to the study of catalytic reactions that use the acid–base properties of PILCs. In general, this type of reaction occurs under thermal and hydrothermal conditions that partially damage the structure of the pillared clay. These aspects are closely related to the relative unsuccessful use of PILCs as catalysts.

More recently, the use of PILCs as catalyst supports for reactions that occur at mild conditions was considered, particularly those involving transition–metal complexes as homogeneous catalysts.[4–6] The heterogenisation of metal complexes with catalytic activity, within inorganic matrices, is a field that has progressed in recent years[7–13] due to the combination of high chemical selectivity and stability, with relatively easier separation of the catalyst from the reaction media. A relevant reaction in organic chemistry that can be catalysed by transition–metal complexes is the alkene epoxidation reaction − the epoxides formed can be transformed into several different products, sometimes under regio- and stereoselective conditions − which is the most recurrent method for direct transfer of oxygen to the alkene; [14,15] manganese(III) complexes with N_2O_2 Schiff base ligands (usually denoted as salen ligands) efficiently catalyse the epoxidation of unfunctionalised alkenes.[16]

When the synthesis of pillared clays is compared, for instance, with the synthesis of large pore zeolites, the former occurs under much milder conditions of temperature and pH than the latter and thus, the integrity of the metal complexes is expected to be preserved under the conditions of PILCs synthesis. This presents the possibility to encapsulate transition metal complexes simultaneously with the pillaring process, a fact that was already shown by us in a previous study using Cu^{II} acetylacetonate based complexes.[4] In this work, we have studied the simultaneous encapsulation of a manganese(III)-salen complex, [Mn(salhd)Cl], (Scheme 1) and the pillaring of a montmorillonite clay with aluminium polyoxycations. The resulting materials were characterised by several techniques, and the catalytic activity assessed in the epoxidation of styrene. To our best knowledge, this is the first work in which the catalytic activity of a complex encapsulated simultaneously with the pillaring process of a clay was studied.

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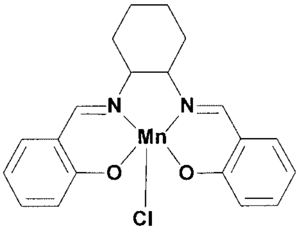

Scheme 1.

Results and Discussion

Material Characterisation

After pillaring (for Al-WYO) or after the pillaring/encapsulation procedure (methods A and B), the solids were calcined at 200 °C; this temperature is lower than that normally used when the main objective is to produce solids with thermally stable pillars ($T = 350–500$ °C). In this study, the calcination temperature was limited by the decomposition temperature of the complexes, which was verified to be above 200 °C. As a consequence, the stability of the pillared materials obtained at this calcination temperature was assessed by X-ray diffraction before and after the Soxhlet extraction step, since it was not clear if such a treatment could induce some changes in the pillars.

In Figure 1 the X-ray diffractograms of the nonencapsulated sample (Al-WYO) and the samples prepared by methods A and B, before and after Soxhlet extraction, are presented; Table 1 summarises the corresponding d_{001} values. Analysis of the diffractograms clearly shows that all the materials are pillared, and this can be confirmed by the increase in the d_{001} value on going from the parent nonpillared clay ($d_{001} = 1.27$ nm)[17] to the pillared materials ($1.78 < d_{001} < 1.92$ nm). Furthermore, from Table 1, it can be seen that: (i) the d_{001} value of Al-WYO is slightly higher than those of the PILCs with encapsulated complexes and, (ii) the d_{001} values of materials subjected to solvent extraction are lower than those of nonextracted materials. The first observation is in contrast with what has been observed in our previous study[4] on the simultaneous pillaring/encapsulation of copper(II) acetylacetonate based complexes, where the larger pentacoordinate complexes have induced an increase in the interlayer distances (acting as templates to the PILC porous structure); the second observation results from some complex exclusion by the purification process. The diffractograms also show, although not in a very pronounced way, that Al-WYO presents a narrower diffraction peak than the samples with metal complexes, which suggest that in the former material the clay particles are better organised.

The isotherms of nitrogen adsorbed at –196 °C in the different samples are presented in Figure 2, and the corresponding values of equivalent surface areas (A_{BET}) and micropore volumes (from t-method[18]) are given in Table 1. The curves show characteristics of isotherm types I and IV, according to the IUPAC classification:[19] they have a steep initial part, typical of microporous solids, but they also present hysteresis. As expected, the A_{BET} and micropore volumes (V_{μ}) of the PILCs with complexes are lower than those found for Al-WYO. Moreover, the solids submitted to solvent extraction show the lowest A_{BET} and V_{μ} values of the series. This result is unexpected, although a similar situation was detected in a previous work.[4] In fact, since the Soxhlet extraction is used to remove the complexes that are physically adsorbed at the external surface, it would be expected that the overall surface area would increase. These results lead us to conclude that during Soxhlet extraction some diffusion of the complexes within the cavities of the pillared clay may occur towards the outer surface (probably as a consequence of concentration gradient), leading to a more obstructed structure.

As mentioned above, the presence of the metal complex within the PILC does not impart major differences in the gallery heights (estimated through XRD data) when Al-WYO is used as a reference. In contrast, the distances between the pillars are very difficult to assess, and in order to obtain additional information on the characterisation of the porosity of the materials, a DFT approach [20,21] was applied to the data from the low-temperature nitrogen adsorp-

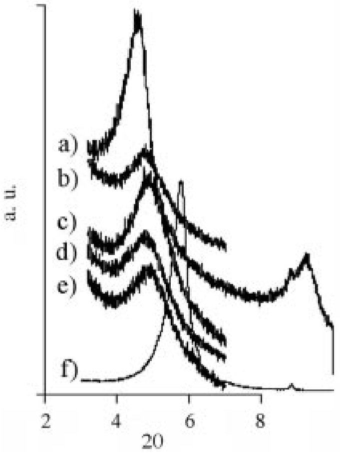

Figure 1. X-ray diffractograms for the Al-WYO sample, a), and for the solids with the [Mn(salhd)Cl] complex encapsulated by method A (b and c) and by method B (d and e). The diffractograms b) and d) refer to samples not subjected to solvent extraction. The curve f) stands for the starting clay.

Table 1. Basal spacing (d_{001}), equivalent surface areas (A_{BET}) and micropore volumes (V_{μ}) by the t-method, from low-temperature nitrogen adsorption. Mn content obtained by atomic absorption spectroscopy (AA) and X-ray photoelectron spectroscopy (XPS).

	d_{001} [nm]	A_{BET} [m^2/g]	V_{μ} [cm^3/g]	Mn content [µmol/g]	
				AA	XPS
Al-WYO	1.93	158	0.055		
Method A (not extracted)	1.84	114	0.027		
Method A (extracted)	1.78	85	0.026	73	68
Method B (not extracted)	1.86	119	0.036		
Method B (extracted)	1.79	61	0.016	71	62
Starting clay	1.27	32	---		

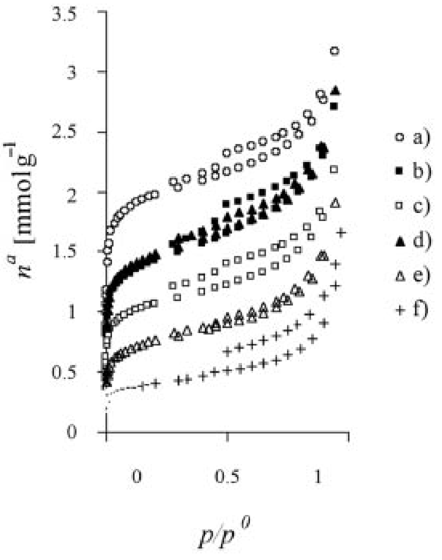

Figure 2. Nitrogen adsorption isotherms at –196 °C for the Al-WYO sample, a), and for the solids with the [Mn(salhd)Cl] complex encapsulated by method A (b and c) and by method B (d and e). The isotherms b) and d) refer to samples not subjected to solvent extraction and the curve f) to the starting clay.

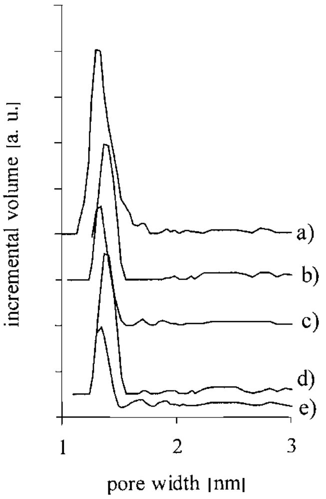

Figure 3. Pore size distributions obtained by DFT for the Al-WYO sample, a), and for the solids with the [Mn(salhd)Cl] complex encapsulated by method A (b and c) and by method B (d and e). The curves b) and d) refer to samples not subjected to solvent extraction.

tion experiments; the results of the pore size distributions obtained in this manner are given in Figure 3. The curves in the micropore region (pore widths <2 nm[19]) cannot be entirely superimposed, and some differences, albeit very small, are expected in the matrix microporosity: the values of the pore widths corresponding to the maximum of the distributions are quite similar for Al-WYO and materials with encapsulated complexes after Soxhlet extraction (1.35 nm), but the distributions obtained for the nonextracted materials are, in fact, slightly shifted to high values. This result has some parallelism with XRD data, and indicates that Soxhlet extraction (removal of adsorbed metal complexes) is essential to the final stabilisation of PILC porosity. We will not pursue the precise significance of the pore widths obtained, since the DFT approach was still not yet widely applied to PILCs; nevertheless, we believe that the results in Figure 3 suggest that the micropore size distribution of materials are, essentially, quite similar, thus confirming that the pillaring process was not significantly perturbed by the presence of the [Mn(salhd)Cl] complex.

Low-resolution XPS spectra of Al-WYO and [Mn(salhd)Cl]@WYO (methods A and B) show the presence of oxygen, silicon, aluminium and magnesium from the aluminium pillared clay lattice at similar values to those published on aluminium pillared clays based on natural Portuguese smectites.[4] The latter materials also show the typical broad Mn 2p$_{3/2}$ bands with maxima at about 642 eV, in agreement with the values reported for manganese(III) complexes with salen[22] and porphyrinic[23] ligands. The most relevant surface contents (Al, Si and Mn) are summarised in Table 2. As can be verified, the Al/Si ratio decreases on going from Al-WYO to those materials with metal complexes: the decrease is slightly larger for the material prepared by method B (19%) than that prepared by method A (9%).

Table 2. XPS results for Al-WYO and metal-complex-based PILCs.

	Atomic-%				
Sample	Al	Si	Mn	Al/Si	Mn/Si
Al-WYO	18.84	15.86		1.19	
[Mn(salhd)Cl]@Al-WYO_A	15.95	14.76	0.13	1.08	0.009
[Mn(salhd)Cl]@Al-WYO_B	15.11	15.81	0.11	0.96	0.007

The bulk Mn content of the samples (obtained by AA, Table 1) indicates that almost 25% of the complex initially added was effectively immobilised in the solid matrix; we emphasise the similarity of the values obtained by both methods (A and B). The surface manganese contents obtained by XPS (Table 2) are similar to those obtained by AA, although slightly lower, suggesting that the complex was encapsulated almost homogeneously, throughout the clay during both simultaneous pillaring/encapsulation methods A and B.

It is worth mentioning that simultaneous pillaring/encapsulation methods (A and B) lead to lower Mn loadings than the in situ synthesis of the metal complex within the aluminium pillared clay.[5] This result may be a consequence of the lower pillaring efficiency of the former methods when compared to the latter as both materials present lower surface aluminium contents than Al-WYO (Table 2). However, this result is in contrast with those obtained for the simultaneous aluminium oxide pillaring and encapsulation of copper(II) Schiff base complexes in a Portuguese montmorillonite, in which encapsulation of these complexes induced not only an increase in the surface aluminium content but also higher PILC basal distances than the corresponding aluminium pillared clay prepared without the presence of complex.[4]

FTIR and UV/Vis Spectroscopy

The FTIR spectra of Al-WYO, the free complex and those of the samples obtained by simultaneous pillaring/encapsulation are shown in Figure 4.Similar to [Mn(salhd)CH_3COO]@Al-WYO prepared by an in situ method[5] and to the aluminium pillared clays based on natural Portuguese smectites (Al-BEN) reported by us,[4] the spectrum of Al-WYO shows intense and large bands due to the clay structure: in the region 3700–3300 cm^{-1} (not shown), which are assigned to the surface hydroxyl groups from the acidic Al–OH group,[24–26] at 1626 cm^{-1} and in the range 1300–400 cm^{-1}, assigned to lattice vibrations[5,23] (asymmetric stretching vibrations of SiO_2 tetrahedra).[25] In addition to these strong bands caused by the parent material, the spectra for [Mn(salhd)Cl]@WYO_A and [Mn(salhd)Cl]-@WYO_B also show bands in the 1600–1200 cm^{-1} region, where the Al-WYO matrix does not absorb (Figure 4), and they may be attributed to the presence of the manganese(III)-salen complex. For clarity, only bands for the samples submitted to solvent extraction (which correspond to materials that have been used in the catalytic experiments described below) are seen in the region 1200–1700 cm^{-1}. Due to the low concentration of metal complex inside the PILC, the bands for the encapsulated complex are difficult to detect, but they can be seen in the range 1400–1500 cm^{-1}. These bands are broader and their frequencies are slightly different from those of the free complex, suggesting that the manganese(III)-salen complex might be distorted as a consequence of the physical constraints imposed by the matrix and/or due to host–guest interactions with the PILC framework within the pores, as observed for copper(II) complexes entrapped in aluminium pillared clays.[4]

The diffuse reflectance UV/Vis spectra of [Mn(salhd)Cl]-@WYO obtained by method A and B (not shown) are very similar to the spectra for the parent Al-WYO in the visible range, where the d-d bands due to the complexes are expected to be seen; however, for $\lambda < 350$ nm, new high-intensity bands are observed that can unambiguously be assigned to the metal complex CT bands. The lack of the d-d bands can be due to two combined factors: (i) the small extinction coefficients associated with these electronic transitions in the manganese(III) complex, and (ii) the dilution effect of the manganese(III)-salen complex within the aluminium pillared clay. Thus, no geometrical information about the entrapped manganese(III)-salen complex can be obtained by its electronic spectra.

Catalytic Experiments

The results of the epoxidation of styrene, at room temperature with the use of the manganese(III)-salen heterogeneous catalysts and PhIO as oxygen source in acetonitrile, are summarised in Table 3 and Figure 5; data from homogeneous-phase and blank experiments run under comparable conditions are also included. These results clearly show that these new catalysts are active in the epoxidation reaction and can be reused for up to four cycles, without significant decrease in the catalytic activity.

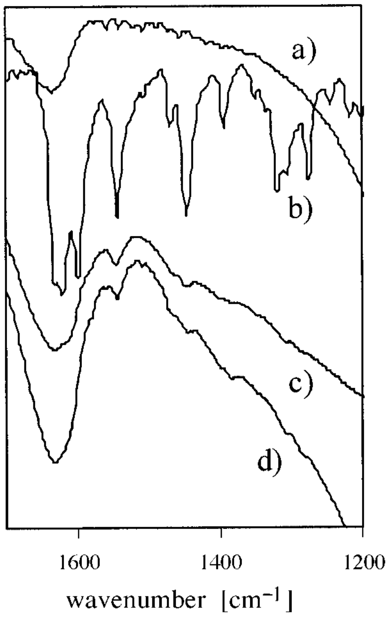

Figure 4. FTIR spectra in the range 1200–1700 cm^{-1} for: a) the Al-WYO pillared clay; b) [Mn(salhd)Cl]; c) and d) are for [Mn(salhd)Cl] encapsulated by methods A and B, respectively.

Both heterogeneous catalysts show high chemoselectivities towards styrene epoxide, which increases slightly with the number of cycles. Nevertheless, these values are lower than that obtained in an experiment run in a homogeneous phase under comparable experimental conditions (Table 3); this may be attributed to some low-extent epoxide-ring opening, owing to support surface acidity and to the higher benzaldehyde selectivity; this occurs by a different catalytic pathway involving the PILC matrix.

The [Mn(salhd)Cl]@Al-WYO_A catalyst shows a styrene conversion quite similar to that of its homogeneous counterpart, whereas for [Mn(salhd)Cl]@Al-WYO_B, styrene conversion is approximately 24% lower. The styrene conversion decreases by 35% and 23% for catalysts prepared by the method A and B, respectively, during further cycles; at the end of the fourth cycle both catalysts show almost the same value. The same trend is observed for the styrene epoxide yield.

Low catalytic activity in the epoxidation of styrene was observed in the filtrate after catalyst removal, indicating that the reaction was not fully catalysed heterogeneously, and that low-extent leaching of the active phase to solution took place; this effect is more perceptible for catalysts obtained by method B. FTIR spectra for both heterogeneous catalysts measured before catalytic reaction and after the fourth cycle show some band intensity decrease in the 1620–1200 cm^{-1} region, which corresponds to the frequency range in which vibration bands for the complex occur; conversely, the bands typical of the Al-WYO matrix do not

Table 3. Epoxidation of styrene catalysed by homogeneous and heterogeneous [Mn(salhd)Cl] complex.[a]

Catalyst	Run	Time[b]	Conversion[c,d]	Selectivity (Yield) [%][d]		
		[h]	[%]	Styrene epoxide	Benzaldehyde	Others[e]
Al-WYO[f]		48	1	16 (0)	84 (1)	0 (0)
[Mn(salhd)Cl]@Al-WYO (method A)	1	48	57	71 (41)	19 (11)	10 (5)
	2	48	41	74 (30)	19 (8)	6 (3)
	3	48	38	75 (28)	20 (8)	5 (2)
	4	48	37	75 (28)	21 (8)	4 (1)
[Mn(salhd)Cl]@Al-WYO (method B)	1	48	47	71 (34)	19 (9)	10 (5)
	2	48	43	72 (31)	20 (9)	8 (3)
	3	48	39	73 (29)	21 (8)	7 (3)
	4	72	36	72 (26)	23 (8)	6 (2)
[Mn(salhd)Cl]		2	62	95 (60)	5 (3)	0 (0)

[a] In acetonitrile, room temperature, molar ratio styrene/PhIO = 2:1. [b] Time needed for total consumption of oxidant, measured by stabilization of the PhI area against PhCl area. [c] Styrene conversion corrected for the limiting reagent, PhIO. [d] Determined by GC-FID against internal standard. [e] Others = other reaction products. [f] Carried out under comparable conditions but with 0.1 g of Al-WYO.

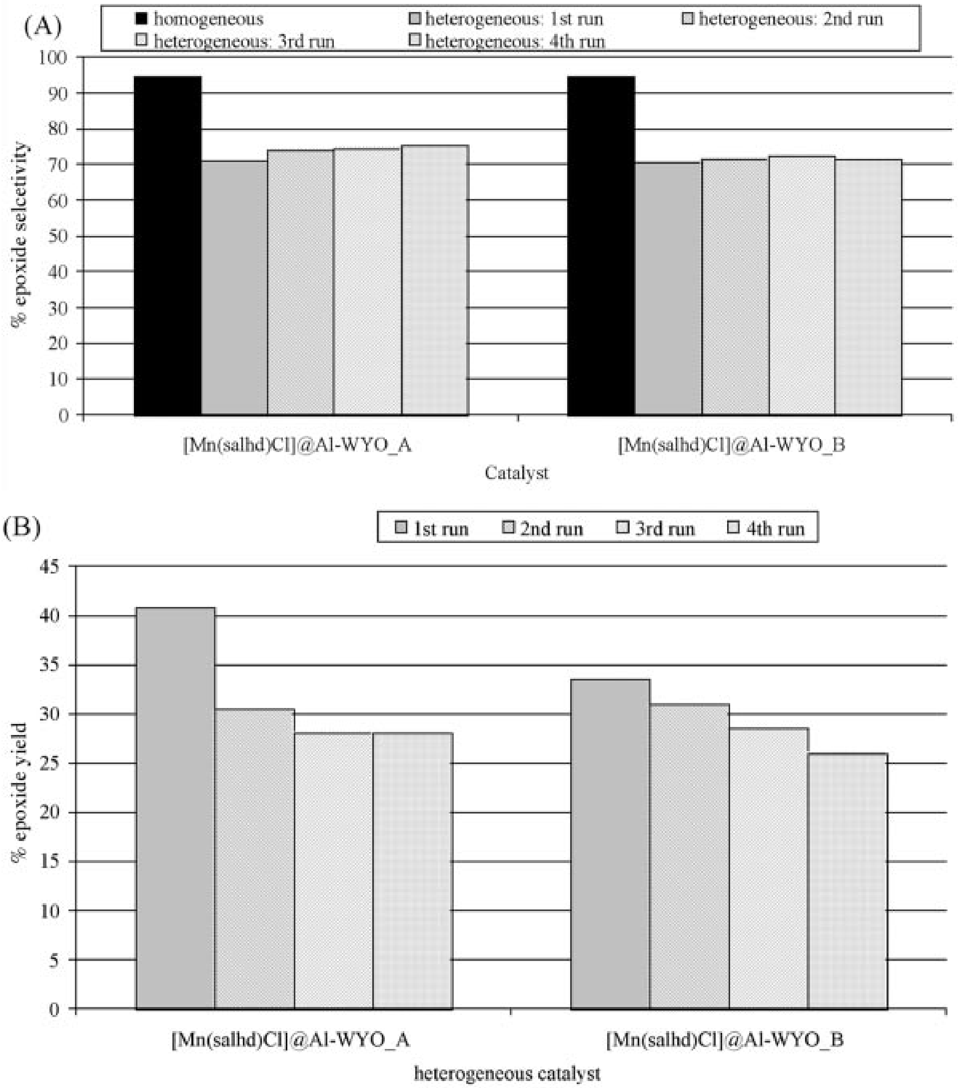

Figure 5. Epoxidation of styrene catalysed by [Mn(salhd)Cl] complex in a homogeneous phase and heterogenised onto the pillared clay: (A) styrene epoxide selectivity [%] and (B) styrene epoxide yield [%).

show significant changes after the catalytic reaction. These observations suggest that no structural changes of the Al-WYO matrix took place during the consecutive catalytic cycles, but some metal-complex leaching must occur in the catalytic experimental conditions. Thus, the styrene epoxide yield decrease with reuse of the heterogeneous catalysts reported herein, might be correlated with some active phase leaching.

In a previous study,[5] we encapsulated, with the use of the in situ method, the same complex within a previously prepared Al-WYO. This catalyst led to comparable styrene conversions, styrene epoxide selectivity and styrene epoxide yields to those with the catalysts described in this work, under the same experimental conditions; however, no metal-complex leaching was detected. The different behaviour exhibited by the materials in which the complexes were immobilised by different procedures can be explained by considering that the pillars are less rigid (these materials are calcined at 200 °C) in the catalysts prepared by using the simultaneous pillaring/encapsulation process, and thus, a higher degree of swelling will occur during catalytic reaction; this will cause the physically entrapped metal complex to leach more easily. In contrast, the material in which the complex was immobilised by in situ synthesis starts from the pre-prepared aluminium pillared clay (calcined at 350 °C), where the higher temperature of calcination confers higher rigidity to the pillars (very low swelling) preventing metal-complex leaching during the catalytic reaction.

Garcia et al. encapsulated the same chiral manganese(III)-salen complex within the zeolite Y, and observed lower styrene epoxide selectivity (61%) than for the homogeneous counterpart (80%), with NaOCl in dichloromethane at 5 °C. This complex encapsulated within Al-WYO, reported herein, gives rise to higher styrene epoxide selectivity (71%) than within the zeolite Y, notwithstanding the different experimental condition used.[27]

It is noteworthy that when the heterogeneous catalysts were used, the reaction time increased and styrene conversion decreased relative to when homogeneous counterparts were used. The first is a general effect that arises upon immobilisation of metal-complex catalyst in porous matrices and has been attributed to diffusion 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.[28] The latter effect, lower styrene conversion, must be due to consumption of PhIO in competing reactions involving the matrix.[29]

Conclusions

New heterogeneous catalysts have been prepared by two different methods based on the simultaneous encapsulation of [Mn(salhd)Cl] and the pillaring process. In both cases, the manganese(III)-salen complex is mainly physically entrapped within the matrix, although some host–guest interactions between the complex and PILC can not be ruled out.

The new materials [Mn(salhd)Cl]@Al-WYO_A and [Mn(salhd)Cl]@Al-WYO_B have been tested in the catalytic epoxidation of styrene at room temperature with PhIO as oxygen source in acetonitrile. The heterogeneous catalysts showed similar styrene conversion to their homogeneous counterparts, high styrene epoxide selectivity and can be reused for at least four times, with a small decrease in their catalytic activity. FTIR spectra of the catalysts after the consecutive catalytic reactions suggest that no structural changes of the PILC occur, but some metal-complex leaching must take place, which is responsible for the small decrease in styrene conversion and styrene epoxide yield in further cycles.

Comparison with results from the literature, obtained with other matrices such as zeolites or MCM type materials, [10–13] is not straightforward. However, we believe that the methodology described in this work can be of interest for the immobilization of large complexes. Moreover, this is a cheap methodology, since by using natural clays as the main host there is no need for expensive silica sources or organic templates. In this way, the results obtained in this work show that the simultaneous encapsulation/pillaring procedure is a useful alternative method for the encapsulation of metal complexes within PILCs, since it produces materials that are stable within the oxidative catalytic media, although some solvent swelling is seen, which is typical of nonpillared clays. To overcome complex leaching induced by the swelling of the material during catalytic reaction, metal complexes must be anchored to the PILC matrix. Research work on complex anchoring to the PILC matrix is in progress and will be published elsewhere.

Experimental Section

Synthesis of the [Mn(salhd)Cl] Complex

The Schiff base ligand *N*,*N'*-*bis*(salicylaldehyde)cyclohexanediamine (H_2salhd) and the corresponding complex chloro-[*N*,*N'*-*bis*(salicylaldehyde)cyclohexanediaminate] manganese(III) ([Mn(salhd)Cl]) were synthesised and characterised as reported elsewhere.[5]

Preparation of the Pillared/Encapsulated Materials

A clay from Wyoming (USA) was used as the starting material. This solid presented a cation exchange capacity of 115 meq/100 g and a structural formula of $(Si_{3.91}Al_{0.09})^{IV}(Al_{1.51}Fe_{0.18}Mg_{0.26})^{VI}(Ca_{/2}, K, Na)_{0.49}$ as described elsewhere.[17,30] The pillaring process was performed using a procedure that was optimised in previous works;[17,30] two solutions were prepared: *solution 1* (which, in fact, is a dispersion) made from clay (1 g) in water (100 mL); and *solution 2*, the oligomer solution. The latter was prepared from aqueous solutions of $AlCl_3$ and NaOH, with an OH/Al ratio of 2, aged for 2 h at 60 °C, after which the pH was increased to 6. The parent pillared clay, denoted as Al-WYO, was prepared by addition of solution 2 dropwise to solution 1 whilst stirring, heated to reflux at 80 °C for 3 h, and kept at 25 °C overnight. The solid was recovered by centrifugation, washed in a dialysis tube until conductivity was lower than 1 mS m^{-1}, freeze-dried and calcined at 200 °C over

2 h after a ramp of 1 °C/min. Several methodologies were tried to encapsulate the complexes, but only the two more successful methods are described. In the procedure, hereafter denoted as *method A*, the [Mn(salhd)Cl] complex (0.5 mmol) was dissolved in ethanol and added to the oligomer solution (solution 2) at a stage at which the oligomeric species had already formed, that is, after the aging and pH adjustment to 6. In the case of *method B*, the complex, also dissolved in ethanol, was added to the clay dispersion (solution 1). In both methods, the amount of ethanol used was in the range 50–70 mL, to ensure that the complex would not precipitate after addition to the aqueous solutions. The remaining experimental steps were the same as described above for the preparation of Al-WYO. After calcination at 200 °C, the samples were Soxhlet extracted to remove the excess complex, first with ethanol and then with dichloromethane until a colourless washing was obtained.

Characterisation Methods

X-ray diffractograms were obtained with oriented mounts,[31] with a Philips PX 1820 instrument using Cu-K_α radiation. Nitrogen adsorption isotherms at –196 °C were measured with an automatic apparatus (Asap 2010; Micromeritics). Before the adsorption experiments the samples were outgassed under vacuum over 2.5 h at 150 °C. FTIR spectra were obtained as KBr pellets (Merck, spectroscopic grade) using a Mattson spectrometer, in the range 1800–1300 cm^{-1}; all spectra were collected at room temperature, with a resolution of 4 cm^{-1} and 32 scans. Metal contents were determined by atomic absorption spectroscopy with 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 performed at "Centro de Materiais da Universidade do Porto" (Portugal), with a VG Scientific ESCALAB 200A spectrometer using a non-monochromatised Mg-K_α 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.

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 i.d.; 0.25 µm film thickness). Conditions used: 60 °C (3 min), 5 °C/min, 170 °C (2 min), 20 °C/min, 200 °C (10 min); injector temperature, 200 °C; detector temperature, 300 °C.

Catalysis Experiments

The catalytic activity of the new materials in the epoxidation of styrene was assessed at room temperature using styrene (substrate, 0.500 mmol), chlorobenzene (GC internal standard, 0.500 mmol), catalyst (0.100 g) and iodosylbenzene (PhIO, 0.250 mmol) as oxidant in of acetonitrile (5.00 cm^3), whilst stirring. During the experiment, aliquots (0.1 cm^3) 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 catalyst was centrifuged. To ensure that the epoxidation was only catalysed heterogeneously, a new portion of PhIO (0.25 mmol) was added to the decanted solution, and the composition of reaction media was remonitored. After use, the catalyst was washed/centrifuged with methanol (five times) and with acetonitrile (two times) to remove occluded reactants and products, and then reused using the same experimental conditions described above. The cycle catalysis/washing was performed three times. The acetonitrile solution (after washing) was checked to verify the existence of styrene. To assess the eventual catalytic activity of the support itself 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); only negligible catalytic activity was found using PhIO as oxidant.

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

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