Direct immobilisation *versus* covalent attachment of a Mn(III)*salen* complex onto an Al-pillared clay and influence in the catalytic epoxidation of styrene

Iwona Kuźniarska-Biernacka [a,b], Ana R. Silva [a], Ana P. Carvalho [c],
João Pires [c,*], Cristina Freire [b,*]

[a] *REQUIMTE, Departamento de Química, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, 4169-007 Porto, Portugal*
[b] *Department of Chemistry, University of Podlasie, 08-110 Siedlce, Poland*
[c] *Departamento de Química e Bioquímica and CQB, Faculdade de Ciências, Universidade de Lisboa,
Ed. C8, Campo Grande, 1749-016 Lisboa, Portugal*

Abstract

A Mn(III)*salen* complex was immobilised onto an aluminium-pillared clay (Al-WYO) by three different methodologies: method A (catalyst A2), direct immobilisation of the complex into the Al-WYO; method B (catalyst A4), covalent anchoring through cyanuric chloride (CC); and method C (catalyst A7), covalent attachment onto a 3-aminopropyltriethoxysilane (APTES) modified Al-WYO mediated by CC. All the materials were characterised by XPS and FTIR; the Mn content of the materials with the immobilised complex was determined by AAS.

FTIR and XPS spectra confirmed the organo-functionalisation of Al-WYO and complex immobilisation in the parent and organo-modified Al-PILCs. Direct immobilisation of the complex into the Al-WYO (method A) leads to the highest immobilisation efficiency ($\eta = 37.5\%$) compared with the anchoring procedures using the two spacers, methods B and C, which gave $\eta = 7.4\%$ and 8.7%. Nevertheless, the surface Mn contents are always higher than those obtained by bulk analysis, suggesting that in all materials the complexes are located within the most external pores.

The Mn(III)*salen*-based pillared clays were tested in catalytic epoxidation reaction of styrene using iodosylbenzene as the oxygen source and were reused for several cycles. The catalyst A2 was the best heterogeneous catalyst among the catalysts prepared since it showed similar substrate conversion and styrene epoxide selectivity to the homogeneous counterpart; the heterogeneous catalysts A4 and A7 showed considerably lower values for these parameters. The styrene epoxide yields decrease in the order, A2 ≫ A4 > A7, which might be associated with some pernicious catalytic activity of the organo-modified supports (A3 and A6). Moreover, A2 could be reused for four times with a slight decrease in its catalytic activity and with almost no leaching of the active phase.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Mn(*salen*) complexes; Pillared clays; Immobilisation; Organo-functionalisation; Covalent attachment; Epoxidation

1. Introduction

The oxidation of olefins to the corresponding epoxide derivatives is of great relevance because these products are important and versatile synthetic intermediates for the chemical industry. Recent studies have demonstrated that manganese(III)*salen* complexes in combination with various oxidising agents successfully catalysed this chemical process [1].

One of the most important challenges in homogeneous catalysis is to transform a successful homogeneous catalyst into a heterogeneous catalytic system, due to the intrinsic advantages of catalyst easy separation and recycling and product separation. Particularly, the heterogenisation of [Mn(*salen*)] complexes also efficiently decreases the formation of the catalytic inactive μ-oxo-Mn(IV) dimers. This is due to the effect of catalyst site isolation and leads to an improvement of the overall catalytic efficiency of the anchored complex when compared to the homogeneous counterpart [2].

Various approaches of immobilisation of Mn(III)*salen* complexes have been reported: complex grafting onto siliceous

---

materials [3], clays [4], pillared clays [5], activated carbons [6], encapsulation into the pores of zeolites [7] and anchoring onto organic polymers [8]. The solid matrixes used have their relative advantages and disadvantages. In the case of pillared clays (PILCs), these materials can be prepared from natural expandable clays (such as montmorillonites) as reviewed elsewhere [9]. In terms of porosity, PILCs present wider pores than zeolites, as Y zeolite for instance, but essentially they are still microporous materials, that is, solids with pores less than 2 nm wide [10]. Considering other properties that are also relevant when using inorganic porous materials as matrixes for the immobilisation of metal complexes, such as hydrophobicity, PILCs have intermediate hydrophobic properties, between zeolites and activated carbons [11]. Another relevant feature of this class of materials to the context of the present work is related with their experimental synthesis. These solids can be prepared in experimental conditions which are not chemically aggressive to the Mn(III)*salen* complexes and therefore in some situations the encapsulation of the complexes can be done simultaneously with the PILCs preparation [5b,c].

In this study a [Mn(*salen*X)] complex functionalised with hydroxyl groups in the aldehyde moiety (Scheme 1) was immobilised onto an aluminium-pillared clay, denoted as Al-WYO, by three different methodologies: method A, direct immobilisation of the complex into the Al-WYO; method B, covalent anchoring through cyanuric chloride (CC); and method C, covalent anchoring through CC onto an 3-aminopropyltriethoxysilane (APTES) modified Al-WYO. The catalytic activity of the immobilised [Mn(*salen*X)] complexes was tested in the catalytic epoxidation of styrene using PhIO as the oxygen source. Using three different procedures to heterogenise the [Mn(*salen*X)] complex onto Al-WYO, we aim to evaluate the influence of the type of immobilisation procedure (direct *versus* covalent grafting) in the catalytic activity of the immobilised complex.

2. Experimental

2.1. Solvents and reagents

Cyanuric chloride (CC), 3-aminopropyltriethoxysilane (APTES), styrene and chlorobenzene were from Aldrich. Iodosylbenzene (PhIO) was synthesised according to procedures described in the literature [12]. All solvents were from Merck, except acetonitrile used in catalytic experiments which was from Romil.

2.2. Preparation of materials

2.2.1. Preparation of the aluminium-pillared clay

A montmorillonite from Wyoming (USA) was used as starting material whose structural formula, based on chemical analysis and cation exchange capacity data, is $(Si_{3.91}Al_{0.09})^{IV}(Al_{1.51}Fe_{0.18}Mg_{0.26})^{VI}(1/2Ca,K,Na)_{0.49}$. This smectite has been extensively characterised in a previous report [13]. The pillared interlayered clay based on WYO, denoted as (Al-WYO), was prepared as described detailed elsewhere [14]. Briefly, 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 2 h after a ramp of 1 °C min^{-1}. The obtained material had a basal spacing (d_{001}) of 1.83 nm and a specific surface area of 270 m^2 g^{-1}.

2.2.2. Functionalisation of Al-WYO with cyanuric chloride (material A3)

The parent material Al-WYO (A1) (0.8 g) was added to a CC saturated solution in dry toluene (50 cm^3) and the resulting mixture was refluxed for 24 h, under inert atmosphere. The solid, A3, was separated by centrifugation, washed with toluene and then with dichloromethane and finally dried overnight at 120 °C, under vacuum.

2.2.3. Functionalisation of Al-WYO with 3-aminopropyltriethoxysilane (material A5)

Al-WYO (A1) (1.0 g) was added to an APTES dry toluene solution (0.3 g, 1.4×10^{-3} mol in 10 cm^3) and the suspension was refluxed for 24 h, under inert atmosphere. The solid, A5, was separated by filtration, Soxhlet extracted with dichloromethane for 48 h and dried overnight at 120 °C in vacuum.

2.2.4. Functionalisation of A5 with CC (material A6)

A suspension of APTES functionalised Al-WYO (A5) (1.0 g) was refluxed for 48 h with a saturated solution of CC in dry toluene (50 cm^3), under inert atmosphere. The solid, A6, was separated by centrifugation, washed with dichloromethane and dried at 120 °C in vacuum for several hours.

2.2.5. Synthesis of [Mn(4-OHsalophen)Cl]

The synthesis and characterisation of the complex [Mn(4-OHsalophen)Cl], chloride-[*N,N'*-bis(4-hydroxysalicylaldehyde)phenylenediiminate] manganese(III), was performed by standard methods and has been reported elsewhere [6a].

$MnC_{20}H_{14}N_2O_4Cl$. FAB-HRMS, *m/z*: calculated ($[MnC_{20}H_{14}N_2O_4–Cl]^+$) 401.0334, experimental 401.0333. FTIR, $\bar{\upsilon}$/cm^{-1}: 1609 s, 1593 s *versus*, 1576 s, 1546 s, 1497 m, 1435 m, 1374 s, 1327 vw, 1254 s, 1207 s, 1194 s, 1142 m, 1127 m, 986 w, 905 w, 848 m, 806 w, 754 m, 658 m, 609 w, 524 w, 496 m, 405 vw.

2.2.6. Complex immobilisation by method A (material A2)

To A1 (2.0 g) was added a 1×10^{-3} mol dm^{-3} solution of [Mn(4-OHsalophen)Cl] in *N,N'*-dimethylformamide and the mixture was refluxed for 30 h. The resulting material, A2, was separated by filtration, Soxhlet extracted with *N,N'*-dimethylformamide until colourless washings were obtained, and then finally dried at 120 °C in vacuum for several hours.

2.2.7. Complex immobilisation by method B (material A4)

The CC-functionalised Al-WYO (A3, 0.6 g) was added to 100 cm^3 of a 1×10^{-3} mol dm^{-3} solution of [Mn(4-OHsalophen)Cl] in dry tetrahydrofuran and the mixture was refluxed for 48 h. The resulting material, A4, was separated by centrifugation, washed with ethanol and dried at 120 °C in vacuum for several hours.
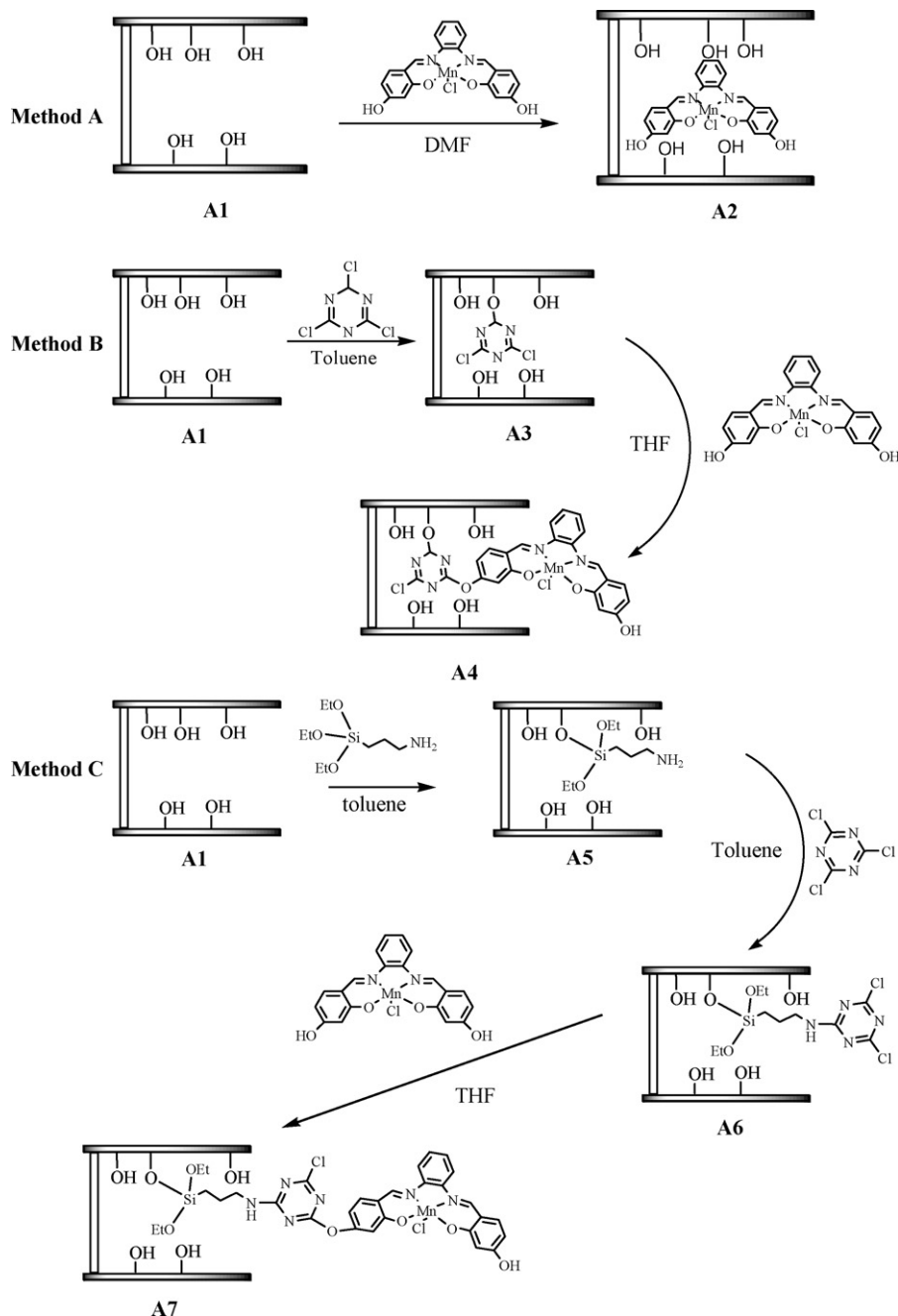
Scheme 1. Immobilisation methods of [Mn(4-OHsalophen)Cl] complex onto Al-WYO materials.

2.2.8. Complex immobilisation by method C (material A7)

The functionalised Al-WYO (A6, 0.6 g) was added to 100 cm^3 of a 1×10^{-3} mol/dm^3 solution of [Mn(4-OHsalophen)Cl] in dry tetrahydrofuran and the mixture was refluxed for 48 h. The resulting material, A7, was separated by centrifugation, washed with dichloromethane, and dried at 120 °C in vacuum, overnight.

2.3. Characterisation methods

The Mn content was determined by atomic absorption spectroscopy in a Pye Unicam SP9 spectrometer. Typically

one sample of 20 mg of solid, previously dried at 100 °C, was mixed with 2 cm^3 of aqua regia and 3 cm^3 of HF for 2 h at 120 °C, in a stainless steel autoclave equipped with a polyethylene-covered beaker (ILC B240). After reaching room temperature the solution was mixed with about 2 g of boric acid and finally adjusted to a known volume with deionised water.

FTIR spectra of the materials were obtained as KBr pellets (Merck, spectroscopic grade) in the range 400–4000 cm^{-1}, with a Jasco FT/IR-460 Plus spectrophotometer; all spectra were collected at room temperature, with a resolution of 4 cm^{-1} and 32 scans. Samples were dried at 120 °C

under reduced pressure for 12 h before recording FTIR spectra.

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 Mg Kα 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 charge of the samples, the C 1s line at 285.0 eV was taken as internal standard. The XPS spectra were fitted using a Gaussian–Lorentzian line shape, Shirley background [15] and damped non-linear least-squares procedure. The line width of Gaussian peak (FWHM, full width at half maximum) was optimised for all components in each individual spectra.

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.

2.4. Catalytic experiments

The catalytic activity of the new materials in the epoxidation of styrene was assessed at room temperature using 5.00×10^{-4} mol of styrene (substrate), 5.00×10^{-4} mol of chlorobenzene (GC internal standard), 0.100 g of heterogeneous catalysts and 2.50×10^{-4} mol iodosylbenzene (PhIO) as oxidant in 5.00 cm^3 of acetonitrile, under stirring conditions. 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 catalyst was removed by centrifugation. To ensure that the epoxidation was only catalysed heterogeneously, a new portion of PhIO (2.50×10^{-4} mol) was added to the filtered solution and the composition of reaction media was re-monitored. After utilisation 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 acetonitrile solution (after washing) has been checked for 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 different supports (0.100 g).

Identification and quantification of products were made by GC-FID analysis (internal standard method). The assignment of the peaks was made by comparison with commercial 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.
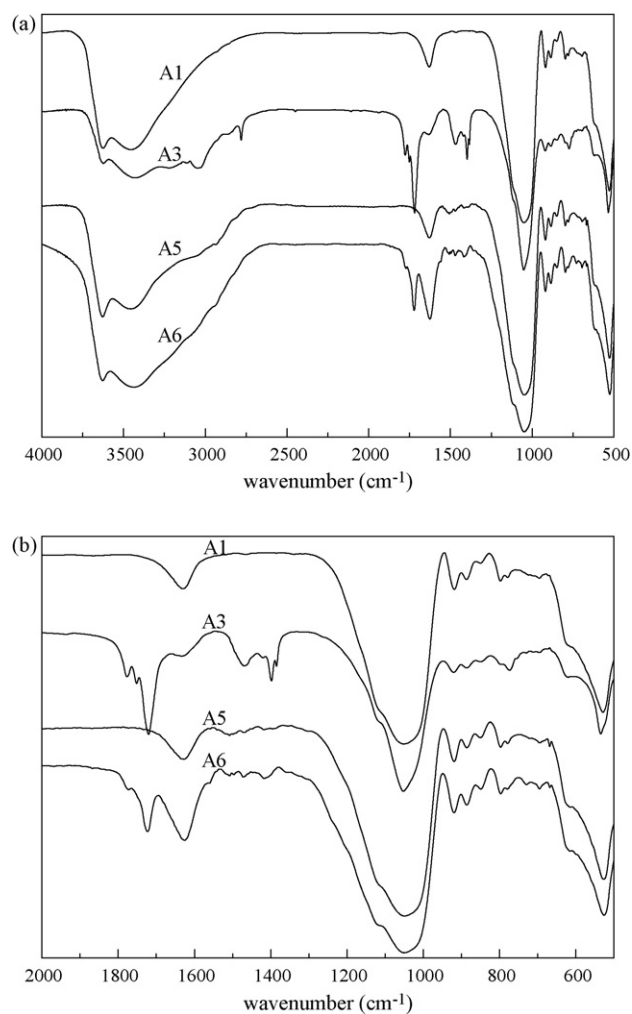

Fig. 1. FTIR spectra of parent (A1) and organo-modified Al-WYO (A3, A5 and A6) in the ranges (a) 4000–500 cm^{-1} and (b) 1800–500 cm^{-1}.

3. Results and discussion

3.1. Characterisation of organo-modified Al-WYO

Fig. 1 shows the FTIR spectra of the parent Al-WYO (A1) and its organo-modified materials A3, A5 and A6. The spectrum of A1 has already been described in details elsewhere [5]. Briefly, the spectrum of Al-WYO shows the typical intense and large band centred at ~3434 cm^{-1}, which is assigned to v(O–H) of the surface hydroxyl groups from the Al–OH, Si–OH groups and physisorbed water. The band at 1630 cm^{-1} is due to physisorbed water (δ(O–H)) and the several bands in the range 1300–400 cm^{-1} are due to clay lattice vibrations (from SiO$_2$ tetrahedra).

Upon grafting of cyanuric chloride (CC) onto Al-WYO (A3 material), several changes in the FTIR spectrum can be observed in all the frequency range. There is an overall intensity decrease of the bands centred at 3434 cm^{-1} and 1630 cm^{-1}, due to the decrease of the physisorbed water on the surface, as a consequence of some hydrolysis reaction with the reactive cyanuric chloride molecules [16,17]. There are several additional peaks at 3219 cm^{-1}, 3108 cm^{-1}, 3050 cm^{-1} and 2781 cm^{-1} which are

due to the anchored CC and its hydrolysis products. In range 2000–1200 cm^{-1}, there are also several bands due anchored CC and its derivatives. The bands at 1777 cm^{-1}, 1749 cm^{-1} and 1720 cm^{-1} are unambiguously assigned to cyanuric acid [16,17], which is the main product of CC hydrolysis reaction. Two others bands at 1467 cm^{-1} and 1398 cm^{-1} are generally associated with the skeleton stretching vibration of C–N heterocyclic rings in CC [18].

As in the functionalisation of Al-WYO with cyanuric chloride, the modification of the pillared clay with APTES (A5) also induces a decrease in the physisorbed water content. This decrease is a consequence of the grafting reaction between the alkoxysilane and the PILCs surface hydroxyl groups [19,20] since water acts as a catalyst for this reaction. The water content lessening is perceived in the decrease in intensity of peaks attributed to ν(O–H) at 3434 cm^{-1} and to δ(O–H) at 1630 cm^{-1}. Nonetheless, the decrease in the former band has also some contribution from the decrease of the peak due to Si–OH groups of the clay, a consequence of the covalent bonding of APTES to these groups *via* the formation of new Si–O–Si–C bonds. These changes were also observed in our previous FTIR study on organo-modification of Laponite clay [4d]. The anchoring of APTES onto Al-WYO also introduced several new bands at 2940 cm^{-1} and 2880 cm^{-1}, which are assigned, respectively, to asymmetric and symmetric vibrations of CH$_2$ units of APTES [21]. Additional evidence of the anchoring of APTES can be gathered by the appearance of peaks in the region 1510–1350 cm^{-1}, which are due to aliphatic C–H bonds [22,23].

Further modification of A5 material with cyanuric chloride (A6 material) leads to a FTIR spectrum different from that of A3 and A5, suggesting that CC has mainly reacted with the APTES grafted to Al-WYO as planned. Nevertheless, some direct reaction of CC with the remaining Si–OH clay groups cannot be excluded. Relative to A5, the FTIR spectrum of A6 shows an increase in the intensity and broadness of the band centred at 3430 cm^{-1} and 1630 cm^{-1}. These observations may suggest some increase in clay water content and a change in the Si–OH groups, but FTIR data do not allow further explanation on these changes. The spectrum of A6 material also shows the same bands as A3 at 1777 cm^{-1} and 1722 cm^{-1} which are assigned to cyanuric acid, the species resulting from the hydrolysis of CC with the clay adsorbed water. This observation suggests that some hydrolysis of cyanuric chloride has also occurred dur-

ing the grafting to APTES modified clay. Among the region 1650–1300 cm^{-1}, the A6 spectrum shows a different band pattern. In this region we expect to see the changes in the APTES aliphatic C–H bend vibrations due to CC grafting and also new bands that can be tentatively assigned to the CC species bound to the amine groups of APTES. Based on the literature data [4d,17] we can state that the new bands of A6 at 1560 cm^{-1}, 1495 cm^{-1} and 1362 cm^{-1} may include the new aliphatic C–H bend vibrations of APTES bound to CC and the ring stretching vibrations of CC bound APTES. The vibration of C–N–R bond which is usually observed around 1130 cm^{-1} could not be detected in A6 since it must be overlapped by the broad band due to Si–O and Si–O–Si stretching vibrations. Finally, the new band at 729 cm^{-1} can be assigned to C–Cl vibrations [4d,17], suggesting that some of the bound CC still have reactive chloride atoms needed for complex anchoring.

In Table 1 are summarised the selected elemental surface atomic contents of all Al-WYO based materials obtained by XPS. The results of the curve fitting for the different high-resolution regions of the XPS spectra are presented in Table 2.

The parent Al-WYO material shows a band in Si 2p region at 102.7 eV that corresponds to silicon from the tetrahedral sheets and a shoulder at 99.8 eV due to silicon from colloidal silica [24]. The symmetrical band at 531.9 eV in the O 1s region is due to single bonded oxygen from clay lattice. The band centred at 74.6 eV in the Al 2p region, is due to the Al^{3+} cations present in the clay sheets and aluminium oxide pillars. Moreover, the low intense and broad bands at 285.0 eV and 288.6 eV in the C 1s region are due to impurities introduced during preparation of the parent material. All these peaks are also observed in modified materials as they are due to intrinsic elements of the clay.

On going from A1 to A3 and to A6 materials there is a decrease on surface oxygen content (Table 1). This is a consequence of the decrease of the clay bound water quantity due to the parallel reaction between the spacers and the physisorbed water. There is also a decrease in aluminium surface contents and Al/Si ratio suggesting the presence of some structural changes within the clay structure upon organo-modification. The aluminium decrease could result from chemical reactions between the products of the spacer hydrolysis reactions (for example HCl in the case of CC anchoring) with Al$_2$O$_3$ from the pillars or/and, less probable, with aluminium from octahedral sheets. Conversely, the Si surface content of A3 is higher than that of

Table 1
Selected XPS results for obtained materials based on Al-WYO

Sample	Atomic (%)							Al/Si	Mn/Si
	C	O	N	Si	Al	Cl	Mn		
A1	8.32	56.55	0.44	15.86	18.84	–	–	1.19	
A2	9.58	52.90	0.89	15.96	16.11	–	0.40	1.01	0.03
A3	9.13	51.9	2.67	17.68	15.78	1.53	–	0.89	
A4	9.82	55.12	1.01	17.32	14.08	1.06	0.11	0.81	0.01
A5	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]	[a]
A6	12.03	45.28	4.63	15.75	13.74	1.77	–	0.87	
A7	15.31	43.45	4.26	15.93	12.90	1.66	0.06	0.81	0.003

[a] A5 sample was not analysed by XPS due to the lack of sample.

Table 2
Curve fitting data of the XPS spectra in the C 1s, O 1s, N 1s, Si 2p, Al 2p, Cl 2p and Mn 2p$_{3/2}$ regions of the Al-WYO materials[a]

	C 1s	O 1s	N 1s	Si 2p	Al 2p	Cl 2p	Mn 2p$_{3/2}$
A1	285.0 (2.7) 288.6 (3.0)	531.9 (2.8)	400.9 (3.6)	99.8 (2.8) 102.7 (2.4)	74.6 (2.4)	–	–
A2	285.0 (2.5) 285.8 (3.0) 288.6 (2.4)	532.3 (2.7)	401.3 (4.0)	100.2 (2.1) 103.0 (2.2)	74.9 (2.2)		642.5 (3.8)
A3	285.0 (2.8) 289.4 (3.8)	532.3 (2.9)	400.5 (3.2)	100.1 (2.3) 102.9 (2.4)	74.9 (2.4)	198.9 (2.8) 200.4 (2.8)	–
A4	285.0 (2.6) 286.6 (2.8) 289.6 (1.4) 292.9 (1.5)	532.3 (2.8)	400.8 (3.0)	100.3 (2.3) 103.1 (2.4)	74.9 (2.5)	198.7 (2.2) 200.3 (2.5)	642.8 (4.2)
A5	b	b	b	b	b	b	b
A6	285.0 (2.1) 286.6 (2.3) 288.9 (2.4)	532.3 (2.8)	399.0 (2.0) 400.3 (2.4) 402.0 (2.0)	100.1 (2.3) 103.0 (2.5)	75.0 (2.3)	198.5 (2.2) 200.4 (2.7) 202.7 (4.1)	–
A7	285.0 (2.0) 286.4 (2.6) 288.8 (2.0)	532.5 (2.8)	400.1 (3.0) 402.3 (2.4)	100.2 (2.4) 103.1 (2.6)	75.1 (2.3)	198.7 (2.5) 200.5 (2.3) 202.4 (2.7)	642.6 (6.0)

[a] Values between brackets refer to the FWHM of the bands.
[b] A5 sample was not analysed by XPS due to the lack of sample.

the parent Al-WYO (A1) material. This is probably an apparent increase, as may be a consequence of the mass loss resulting from the disruption of some aluminium oxide pillars, as referred above.

Compared with A1, the materials A3 and A6 also show an increase in carbon and nitrogen atomic contents, as well as presence of chloride, confirming the presence of the anchored cyanuric chloride in both materials. The experimental N:Cl surface atomic ratio obtained for A3 and A6 materials are, respectively, 1.7 and 2.6, indicating that there are still chloride atoms in both materials to react with the Mn(III)*salen* complex. The higher N/Cl ratio in A6 than in A3 suggests that, effectively, the cyanuric chloride was anchored onto the APTES.

In the C 1s region of A3 spectrum there are two peaks, one at 285.0 eV, which is attributed to the contamination of the parent material and another at 289.4 eV, assigned to bounded CC and possible triazine dimers [16,25]. The latter peak confirms the anchorage of CC directly onto the clay surface. Nevertheless, this peak is quite large (Table 2), what suggests that it may include some contribution of the peak due to cyanuric acid (the main product of CC hydrolysis), as confirmed by the FTIR data. For A6, the confirmation that cyanuric chloride has mainly reacted with the grafted APTES arises from the new peak in the spectrum in the C 1s region. This peak has a BE = 288.8 eV, and can be assigned to APTES-N-CC, since it is similar to that observed for the attachment of *o*-toluidine onto CC graphitic modified electrodes [16] and is lower than that observed in A3 for direct anchoring of CC onto the pillared clay, Si–O–CC.

In the N 1s region of A3 material there is only one broad band at BE = 400.5 eV, typical of sp^2 C=N bond [18] and assigned to the nitrogen of the CC aromatic ring. For A6, the spectrum in the N 1s region shows one unsymmetrical band at

400.5 eV that could be resolved onto three components. Two of the deconvolved peaks have binding energies (BE) at 399.0 eV and 400.3 eV, which are similar to typical BE values for sp^3 C–N and sp^2 C=N bonds [18], and thus can be assigned to nitrogen from APTES and CC, respectively. The third peak at BE = 402.0 eV can correspond to NH$_3^+$ groups [26] obtained from the protonation of the free NH$_2$ by HCl resulting from reaction between CC and APTES.

3.2. Characterisation of [Mn(4-HOsalophen)]-based PILCs

The immobilisation of manganese complex onto Al-WYO materials (A2, A4 and A7) was confirmed by Mn bulk analysis (Table 3) and high-resolution XPS spectra in Mn 2p region, which shows a broad band at 642.5 eV typical for Mn(III)*salen* type complexes (Tables 1 and 2).

The Mn bulk content and immobilisation efficiency decrease in the order A2 > A7 ≈ A4. These results show that the use of spacers drastically decreased the amount of immobilised complex. Furthermore, the size and rigidity of the spacers do not have a significant influence in the amount of immobilised complex, since A4 and A7 have similar immobilisation efficiency. Considering the values of Mn bulk contents in all materials, these are significantly lower than those of Mn surface content estimated by XPS (Table 3), reflecting a preference of the complex for being immobilised within the most external porosity.

All methods of complex immobilisation (methods A–C) lead to similar changes in the elemental surface contents, namely, decreases in the Al and O content and increases in carbon and nitrogen content. The latter increases confirm the presence of the complex in all supports, but the decrease in O and Al content can

Table 3
Mn contents, determined by atomic absorption spectroscopy, in as-prepared materials and after the catalytic tests

Sample	As prepared material[a,b]	After catalytic test[a,b]	XPS[b,c]	Efficiency of immobilisation (%)[d]
A2	84	80	299	37.5
A4	18	89	148	7.4
A7	20	79	64	8.7

[a] Determined by AAS.

[b] Mn content in $\mu mol \times g^{-1}$.

[c] Mn amount per weight of sample (before catalytic tests) calculated from XPS data in Table 1: mmol Mn/weight of sample = at% Mn/[at% C × Ar(C) + at% N × Ar(N) + at% O × Ar(O) + at% Si × Ar(Si) + at% Al × Ar(Al) + at% Cl × Ar(Cl) + at% Mn × Ar(Mn) + at% Na × Ar(Na)].

[d] Mn bulk content/Mn used in the immobilisation reaction × 100.

be associated with some disruption of aluminium oxide pillars as a consequence of the complex immobilisation.

In the C1s region of A2 (method A) a new band appears at 285.8 eV, which could be assigned to the presence of complex. The binding energy (BE) values of bands in O 1s, Si 2p and Al 2p regions are similar to those of the parent PILCs, which suggest the absence of strong complex interactions with the parent-pillared clay.

After complex anchoring onto the A3, material A4 (method B) there is a decrease in the chloride content of the samples. This is most probably due to the occurrence of a reaction between the hydroxyl groups of the complex and the reactive chlorines from bound CC, leading to the formation of an ether bond between the support and the Mn complex, as described in [16]. The BE values of the typical pillared clay bands remain unchanged indicating no major modifications within the clay structure.

For complex immobilisation onto A6, material A7 (method C), there is also a decrease in chloride surface content and no change in the BE values of the pillared clay bands. This suggests that the reaction of the complex with Al-WYO modified sequentially by APTES and CC took place preferentially through the formation of an ether bond between CC and the complex, as in A4 [16].

Fig. 2. FTIR spectra of Al-WYO with immobilised complex (A2, A4 and A7) in the ranges (a) 4000–500 cm^{-1}; (b) 1850–500 cm^{-1} in both panels; (c) corresponds to the FTIR spectrum of the complex.

The materials with the immobilised complex were also characterised by FTIR and their spectra are depicted in Fig. 2, jointly with that of the free complex. The most significant differences between the spectra of the materials with the immobilised complexes and their corresponding supports are detected in the region 1600–1275 cm^{-1}. This frequency range corresponds to the region where the most important and intense bands from the complex are observed and the Al-WYO has no absorptions. Nevertheless vibrations due to spacers are also present in this region what renders difficult the assignment of complex bands (A4 and A7).

In A2 material the bands observed in the frequency range 1600–1275 cm^{-1} are unequivocally assigned to the immobilised complex, since no spacer has been used in the immobilising procedure. These bands have frequencies that are quite similar to those of the free complex (see Section 2) [6a]: 1542 cm^{-1}, 1471 cm^{-1}, 1448 cm^{-1}, 1383 cm^{-1}, 1309 cm^{-1} and 1283 cm^{-1}, suggesting that the interaction of the complex with the support should take place through the metal centre and no significant distortions occurs in the complex upon its direct immobilisation.

The band assignment in the FTIR spectra of A4 and A7 materials is more difficult due to the low spectral resolution and presence of the spacer vibrations bands. Nevertheless, it is possible to notice some frequency changes in the bands of the grafted spacers upon complex immobilisation, indirectly suggesting that the complex has been anchored through them.

3.3. Catalytic activity

The manganese(III)*salen* heterogeneous catalysts were tested in styrene epoxidation in acetonitrile using PhIO as an oxygen source. The results obtained are summarised in Table 4 and Fig. 3, where the data from the homogeneous phase and the blank experiments run under comparable conditions are also included.

Both types of catalysts, that is, the one obtained by direct immobilisation (A2) and those obtained by covalent attachment (A4 and A7) are active in the epoxidation of styrene. The styrene epoxide selectivity of A2 is high and comparable to the reaction run in homogeneous phase, under similar experimental conditions, but A4 and A7 show much lower styrene epoxide selectivity values (Table 4 and Fig. 3). The lower selectivity values for A4 and A7 result from the catalytic activity of the supports themselves that, in both cases, are quite significant towards benzaldehyde and other by-products (Table 4). Simi-
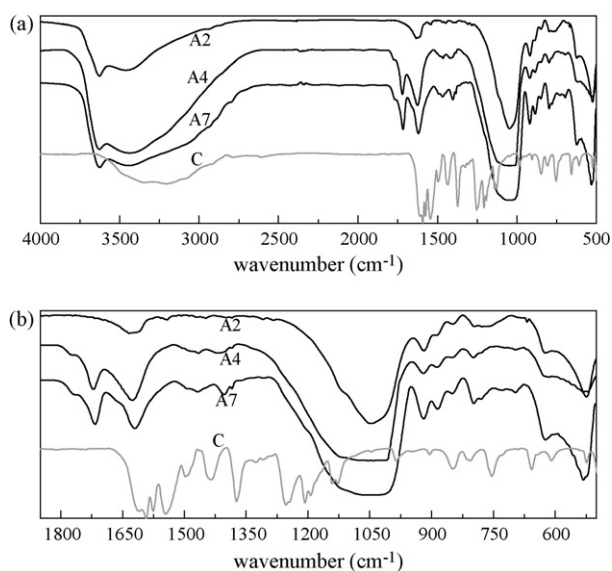
Table 4
Epoxidation of styrene catalysed by homogeneous and heterogenised [Mn(4-OHsalophen)Cl] complex[a]

Catalyst	%Mn[b]	Cycle	t (h)[c]	%C[d,e]	% Selectivity[e,f]			% Yield[e,f]	TON[g]	TOF (h^{-1})[h]
					SE	B	O	SE		
Homogeneous	0.5		42	89	92	8	0	82	20	0.5
	1.7		3	49	90	9	1	44	8	2.7
A2	1.8	1	48	35	80	18	2	28	5	0.1
		2	48	36	73	22	5	27	5	0.1
		3	48	35	73	21	5	26	9	0.2
		4	48	27	70	26	4	19	8	0.2
A4	0.4	1	48	38	29	53	18	11	i	i
		2	48	22	46	53	1	10	i	i
		3	73	21	49	51	0	10	i	i
A7	0.3	1	72	46	18	42	40	8	i	i
		2	72	14	37	63	0	5	i	i
A1[j]			48	1	16	84	0	0		
A3[j]			72	25	8	66	26	2		
A6[j]			72	28	6	56	38	2		

[a] In acetonitrile, at room temperature, molar ratio styrene/PhIO = 2:1.
[b] % of Mn relative to styrene.
[c] Time need for complete consumption of oxidant.
[d] Styrene conversion corrected for the limiting reagent (PhIO).
[e] Determined by GC-FID against internal standard (chlorobenzene).
[f] SE = styrene epoxide, B = benzaldehyde and O = other reaction products.
[g] Total TON = mmol epoxide/mmol Mn.
[h] TOF = TON/reaction time.
[i] Not calculated due to the significant change in Mn% during catalytic cycles (see Table 3).
[j] Carried out under comparable experimental conditions but with 0.1 g of supporting material.

larly, the styrene conversion (%C) of A2, when compared to the homogenous analogous reaction is 29% lower, but the other catalysts A4 and A7 show a higher decrease, 57% and 48%, respectively. As a consequence of their styrene conversion values, the catalyst A2 was reused three times, whereas catalysts A4 and A7 were only recycled two and one more time, respectively.

The decrease in the substrate conversion and increase in reaction time, usually observed upon immobilisation of molecular catalysts into porous supports, can have two main causes. The first is related with diffusion restrictions of the substrate through the porous structure of the support, and in this particular case, the diffusion of the reactants to the metal centre can be particularly hindered for PhIO, which is solid and has low solubility

Fig. 3. Styrene epoxide selectivity % in the catalytic reactions of free and immobilised [Mn(4-OHsalophen)Cl] complex.

in acetonitrile, its solubilisation being controlled by its rate of consumption [27]. The second cause are the electronic changes induced in the metal centre through the chemical modifications of the ligands/metal centre as a consequence of the immobilisation procedures used. This latter effect may have an important contribution for catalysts A4 and A7.

During the catalyst reuse of A2 there was a small reduction of the styrene conversion and epoxide selectivity since, at the end of the fourth cycle the values were, respectively 20% and 12% lower than initial values. Conversely, for A4 and A7, the decrease in the styrene conversion was 43% and 70%, respectively, at the end of the second cycle. In order to get more insights into the recycled catalysts the Mn bulk content was determined and FTIR spectra obtained.

The bulk manganese content of the A2 catalyst after the last reutilisation (Table 3) is quite similar to the one obtained before the catalytic reactions, indicating that no significant leaching of the active phase took place: the direct interaction of the complex and the pillared clay was stable in the catalytic reaction media. For A4 and A7 catalysts, there was an increase in the Mn contents, similarly to our previous study on immobilisation of chiral manganese(III)*salen* complexes onto pillared clays [5d]. This increase in Mn content is apparent and may be related with the collapsing of some of pillars or/and decomposition of spacers during catalytic reaction, which makes the mass of the sample to decrease and thus, indirectly, increasing the manganese content. Some confirmation for this can be gathered from FTIR spectra collected after the last reaction cycle and its comparison with the spectra obtained before the catalytic reaction (Fig. 4).
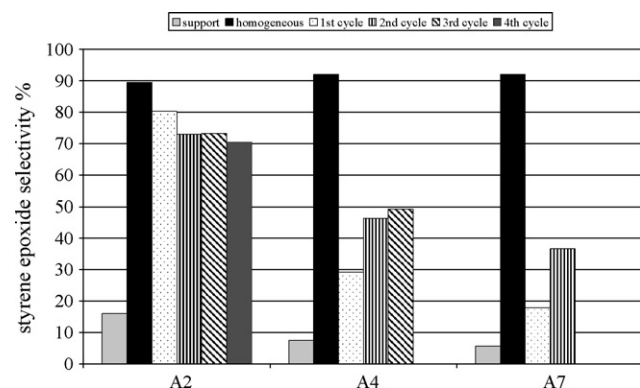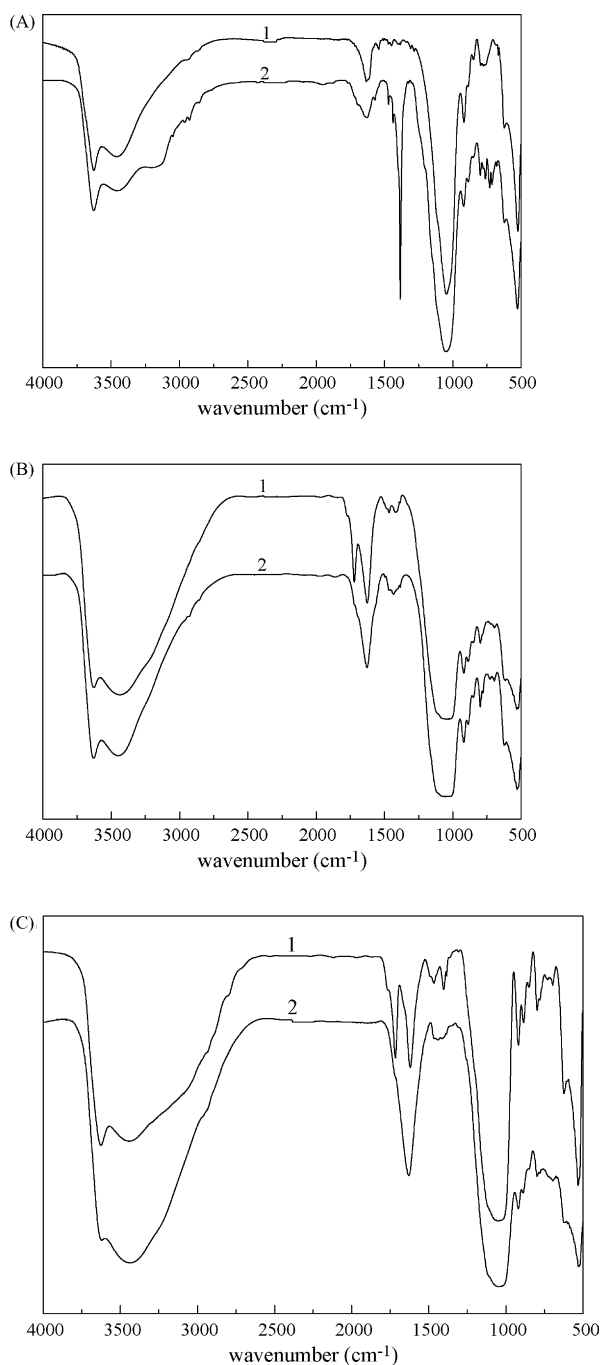
Fig. 4. FTIR spectra of [Mn(4-OHsalophen)Cl]-based Al-WYO materials after catalysis: (A) A2, (B) A4 and (C) A7 before (curve 1) and after the last catalytic cycle (curve 2).

FTIR spectrum of A2 (Fig. 4A), after the last catalytic cycle, shows the broadening of band at $1283 \, cm^{-1}$, a new band at $1385 \, cm^{-1}$, and some changes in $760–713 \, cm^{-1}$ and $3300–2800 \, cm^{-1}$ ranges. The positions of new bands and shoulders suggest presence of occluded oxidant inside the porous of A2, which has not been removed during the washing–centrifugation process. Beside this, we cannot exclude some metal complex decomposition, by partial oxidation [28], under the catalytic experimental conditions. Thus, the observed styrene epoxide yield decrease, especially during the last reuse

of A2 catalyst, might be correlated with deactivation of the active phase.

The comparison of the FTIR spectra of A4 and A7 heterogeneous catalysts before and after the last reaction cycle (Fig. 4B and C) show some significant changes in the range $1750–1200 \, cm^{-1}$ region. In fact, the intensity of the band due to the cyanuric acid decreased, probably as a consequence of the catalytic reaction media and the bands due to the spacers/complex become less resolved, suggesting some decomposition of the complex and spacers. Nonetheless, the lack of resolution of the bands due to the clay structure prevents the use of FTIR to confirm the collapsing of some aluminium pillars suggested by AAS data. It can be concluded that, in contrast with our previous results on the immobilisation of this complex onto a Laponite clay using these three anchoring procedures [4D], the use of the spacers in this particular case, did not improve the catalytic properties of the anchored complex and, therefore, its direct immobilisation into the PILCs porous structure conducted to the best results. It is noteworthy that we had already reported that Mn(III)salen catalysts encapsulated onto PILCs to be an efficient, highly chemoselective and reusable heterogeneous catalysts in the room temperature epoxidation of alkenes [5].

4. Conclusions

Three new heterogeneous catalysts have been prepared by immobilisation of [Mn(4-OHsalophen)Cl] complex onto Al-WYO clay by three different methodologies: direct immobilisation (method A) and anchoring through spacers, such as cyanuric acid and 3-aminopropyltriethoxysilane (methods B and C). The immobilisation methods lead to different anchoring efficiency, with method A being considerably more effective, $\eta = 37.5$, than methods B and C with $\eta = 8.7\%$ and 7.4%, respectively.

The heterogeneous catalysts showed similar (A2) and lower (A4 and A7) styrene epoxide selectivity than their homogeneous counterparts. Moreover, A2 catalysts could be reused for four times with a small decrease in its catalytic activity and with almost no leaching of the active phase. Catalysts A4 and A7 were reused only twice due to their lower substrate conversion. The active phase leaching of A4 and A7 catalysts could not be evaluated as some disruption of the pillars might have occurred. The styrene epoxide yields decrease in the order: $A2 \gg A4 > A7$, which is related with some pernicious catalytic activity of the organo-modified supports. In conclusion, the direct immobilisation of the complex [Mn(4-OHsalophen)Cl] into Al-WYO was shown to be more effective than those using spacers (organo functionalised Al-WYO), not only in terms of its preparation, but also in its stability in the catalytic reaction media.

References

[1] (a) T. Katsuki, Coord. Chem. Rev. 140 (1995) 189–214;
(b) E.N. Jacobsen, M.H. Wu, in: A. Pfaltz, E.N. Jacobsen, H. Yamamoto (Eds.), Comprehensive Asymmetric Catalysis, Springer-Verlag, Berlin, 1999, pp. 649–677.

[2] Q.H. Fan, Y.M. Li, A.S.C. Chan, Chem. Rev. 102 (2002) 3385–3465.

[3] (a) B.M. Choudary, N.S. Chowdari, M.L. Kantam, P.L. Santi, Catal. Lett. 76 (2001) 213–218;
(b) D.W. Park, S.D. Choi, S.J. Choi, C.Y. Lee, G.J. Kim, Catal. Lett. 78 (2002) 145–151;
(c) H. Zhang, S. Xiang, C. Li, Chem. Commun. (2005) 1209–1211;
(d) F. Bigi, L. Moroni, R. Maggi, G. Sartori, Chem. Commun. (2002) 716–717;
(e) P. Piaggio, C. Langham, P. McMorn, D. Bethell, P.C. Bulman-Page, F.E. Hancock, C. Sly, G.J. Hutchings, J. Chem. Soc., Perkin Trans. 2502 (2000) 143–148.

[4] (a) R.I. Kureshy, N.H. Khan, S.H.R. Abdi, I. Ahmad, S. Singh, R.V. Jasra, Catal. Lett. 91 (2003) 207–210;
(b) R.I. Kureshy, N.H. Khan, S.H.R. Abdi, I. Ahmad, S. Singh, R.V. Jasra, J. Catal. 221 (2004) 234–240;
(c) S. Bhattacharjee, T.J. Dines, J.A. Anderson, J. Catal. 225 (2004) 398–407;
(d) I. Kuźniarska-Biernacka, A.R. Silva, A.P. Carvalho, J. Pires, C. Freire, Langmuir 21 (2005) 10825–10834.

[5] (a) I. Kuźniarska-Biernacka, A.R. Silva, R. Ferreira, A.P. Carvalho, J. Pires, M.B. Carvalho, C. Freire, B. de Castro, New J. Chem. 28 (2004) 853–858;
(b) B. Cardoso, J. Pires, A.P. Carvalho, M.B. Carvalho, I. Kuźniarska-Biernacka, A.R. Silva, C. Freire, B. de Castro, Eur. J. Inorg. Chem. (2005) 837–844;
(c) B. Cardoso, J. Pires, A.P. Carvalho, I. Kuźniarska-Biernacka, A.R. Silva, B. de Castro, C. Freire, Micropor. Mesopor. Mater. 86 (2005) 295–302;
(d) P. Das, I. Kuźniarska-Biernacka, A.R. Silva, A.P. Carvalho, J. Pires, C. Freire, J. Mol. Catal. A: Chem. 248 (2006) 135–143.

[6] (a) A.R. Silva, J.L. Figueiredo, C. Freire, B. de Castro, Micropor. Mesopor. Mater. 68 (2004) 83–89;
(b) A.R. Silva, C. Freire, B. de Castro, Carbon 42 (2004) 3027–3030;
(c) A.R. Silva, V. Budarin, J.H. Clark, B. de Castro, C. Freire, Carbon 43 (2005) 2096–2105.

[7] G. Gbery, A. Zsigmond, K.J. Balkus Jr., Catal. Lett. 74 (2001) 77–80.

[8] (a) K. Smith, C.H. Liu, Chem. Commun. (2002) 886–887;
(b) L. Canali, F. Cowan, H. Deleuze, C.L. Gibson, D.C. Sherrington, J. Chem. Soc., Perkin Trans. 1 (2000) 2055–2066;
(c) H. Zhang, S. Xiang, J. Ciao, C. Li, J. Mol. Catal. A: Chem. 238 (2005) 175–184;
(d) H. Zhang, Y. Zhang, C. Li, Tetrahedron-Asymmetr. 16 (2005) 2417–2423.

[9] A. Gil, L.M. Gandía, M.A. Vicente, Catal. Rev. -Sci. Eng. 42 (2000) 145–212.

[10] K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Rouquerol, T. Siemieniewska, Pure Appl. Chem. 57 (1985) 603–619.

[11] J. Pires, M.L. Pinto, A. Carvalho, M. Carvalho, Adsorption 9 (2003) 303–309.

[12] P. Piaggio, P. McMorn, D. Murphy, D. Bethell, P.C. Bulman-Page, F.E. Hancock, C. Sly, O.J. Kertoon, G.J. Hutchings, J. Chem. Soc., Perkin Trans. 22 (2000) 2008–2015.

[13] J.M. Guil, J.A. Perdigón-Melón, M.B. de Carvalho, A.P. Carvalho, J. Pires, Micropor. Mesopor. Mater. 51 (2002) 145–154.

[14] J. Pires, M.B. de Carvalho, A.P. Carvalho, Zeolites 19 (1997) 107–113.

[15] D.A. Shirley, Phys. Rev. B 5 (1972) 4709–4714.

[16] M.F. Dautartas, J.F. Evans, T. Kuwana, Anal. Chem. 51 (1979) 104–110.

[17] S. Samaritani, P. Peluso, C. Malanga, R. Menicagli, Eur. J. Org. Chem. (2002) 1551–1555.

[18] C. Li, C.-B. Cao, H.-S. Zhu, Mater. Lett. 58 (2004) 1903–1906.

[19] L.D. White, C.P. Tripp, J. Colloid Interface Sci. 232 (2000) 400–407.

[20] J.C. Hicks, R. Dabestani, A.C. Buchanan III, C.W. Jones, Chem. Mater. 18 (2006) 5022–5032.

[21] S. Zheng, L. Gao, J. Guo, Mater. Chem. Phys. 71 (2001) 174–178.

[22] N.N. Herrera, J.-M. Letoffe, J.-P. Reymond, E. Bourgeat-Lami, J. Mater. Chem. 15 (2005) 863–871.

[23] A.B. Bourlinos, D.D. Jiang, E.P. Giannelis, Chem. Mater. 16 (2004) 2404–2410.

[24] D. Zhao, Y. Yang, X. Guo, Inorg. Chem. 31 (1992) 4727–4732.

[25] S. Dieckhoff, V. Schlett, W. Possart, O.-D. Hennemann, J. Günster, V. Kempter, Appl. Surf. Sci. 103 (1996) 221–229.

[26] A.S. Maria Chong, X.S. Zhao, J. Phys. Chem. B 107 (2003) 12650–12657.

[27] B.B. De, B.B. Lohray, S. Sivaram, P.K. Dhal, Macromolecules 27 (1994) 1291–1296.

[28] J.M. Fraile, J.I. Garcýa, J. Massam, J.A. Mayoral, J. Mol. Catal. A: Chem. 136 (1998) 47–57.