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Article

K10-Montmorillonite as Support for a Cationic Manganese(III)-*salen* Complex

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A argila K10, uma montmorilonita comercial, foi usada como suporte para a imobilização de um complexo catiônico do tipo manganês(III)-*salen*, o qual apresenta propriedades catalíticas na reação de epoxidação de alcenos. O complexo imobilizado na argila K10 foi testado na epoxidação de três alcenos (estireno, α-metilestireno e 6-ciano-2,2-dimetilcromeno) a 0 ºC, usando três sistemas oxidantes diferentes. Todas as amostras, antes e depois dos ensaios catalíticos, foram caracterizadas por várias técnicas, como adsorção de nitrogênio a baixa temperatura, DRX e FTIR. Foi ainda efetuada a análise química dos catalisadores, por espectroscopia de absorção atômica e por XPS, com o objetivo de avaliar a influência de cada sistema substrato/oxidante na integridade do respectivo catalisador. Os resultados catalíticos demonstraram uma forte influência do sistema substrato/oxidante na percentagem de excesso enantiomérico (*%ee*). Em alguns casos, os valores de *%ee* são comparáveis aos valores obtidos em fase homogênea. Os resultados também realçam a necessidade de otimização dos sistemas oxidantes, uma vez que alguns dos oxidantes usualmente utilizados podem conduzir à decomposição do complexo imobilizado, com a consequente lixiviação da fase ativa e desativação do catalisador.

A commercial K10-montmorillonite was used as support for the immobilization of a cationic manganese(III)-*salen* complex. The catalytic behavior of the resulting material was tested in the enantioselective epoxidation of three different alkenes, *viz.:* styrene, α-methylstyrene and 6-cyano-2,2-dimethylchromene, at 0 ºC, using three different oxidant systems: *m*-chloroperoxybenzoic acid (*m*-CPBA) and *N*-methylmorpholine (NMO) as co-oxidant, iodosylbenzene (PhIO) and sodium hypochlorite. All samples, before and after the catalytic studies, were characterised by nitrogen adsorption at −196 ºC, DRX, FTIR and chemical analysis, in order to evaluate the influence of the substrate/oxidant system on catalyst integrity. The catalytic results demonstrated a strong influence of the substrate and oxidant system on the enantiomeric excess (*%ee*) values. In some cases, these values were comparable to those in the corresponding homogeneous phase reactions. The results also highlighted the importance of optimizing the oxidant systems, since they may lead to the disruption of the complex from the support, and the consequent catalyst deactivation.

Keywords: K10-montmorillonite; alkene epoxidation, catalyst support, manganese(III)-salen

Introduction

Chiral manganese(III) complexes have been a subject of current interest due to their wide possibilities as catalysts in asymmetric epoxidation of alkenes, as reviewed by Song and Lee.[1] Several manganese(III) complexes have been developed, which have shown excellent results for enantioselective catalytic reactions in homogeneous phase.[1,2] These complexes are, essentially, manganese(III)-*salen* complexes, where *salen* denotes a family of N_2O_2-type tetradentate Schiff base ligands obtained by condensation between a salicylaldehyde derivative and a (chiral) diamine.[3]

However, the relative high cost of these complexes and the lack of efficient methodologies for their recycling and reuse limit their applications in industrial scale. In this sense, several studies have been carried out in order to develop efficient methods for catalysts reuse. One of the

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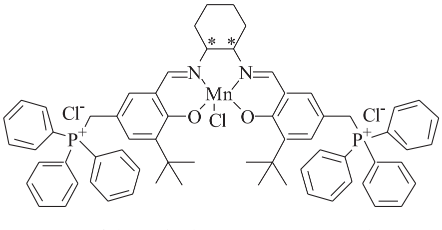
*e-mail: jpsilva@fc.ul.pt; acfreire@fc.up.pt approaches is the metal complexes immobilization in solid matrixes, namely organic and inorganic, porous and non-porous, as reviewed elsewhere.[1,3] Natural and synthetic clays have been used as supports for complexes with catalytic activity,[4-6] and in some cases may lead to positive effects in the enantioselectivity due to their anionic lamellar nature.[7] Nevertheless, the use of commercial clays, with the advantages of working with commercially available materials, such as K10-montmorillonite, as supports for enantioselective cationic manganese(III)-*salen* complexes, has received limited attention in the literature.[8,9] In the present work, we studied the role of commercial K10-montmorillonite as support for a cationic manganese(III)-*salen* complex derived from Jacobsen catalyst. The catalytic behavior of the immobilised catalyst was ascertained in epoxidation reactions of various alkenes, *i.e.*, styrene, α-methylstyrene (α-Me-styrene) and 6-cyano-2,2-dimethylchromene (6-CN-chromene). The resulting epoxide, produced from these reactions, can be used in several important reactions of fine chemistry.

Experimental

Catalyst preparation

The synthesis of chiral [(*R,R*)-*N,N'*-bis(3-tert-butyl-5-((triphenylphosphonium)-methyl)salicylidene)-1,2-cyclohexanediaminechloride]-manganese(III)chloride, henceforth labelled as C1, was based on the literature.[10] Briefly, the Schiff base (0.9 g; 1.8 mmol) was dissolved in absolute ethanol (30 cm^3) and manganese(II) chloride tetrahydrate (0.36 g; 1.8 mmol) was added; the resulting mixture was stirred under reflux for 2 h. A brown solid, C1 (see Scheme 1), was obtained with a 59% yield.



Scheme 1. Structure of the cationic manganese(III)-*salen* complex (C1).

K10-montmorillonite was obtained from Aldrich and was dehydrated at 120 °C under reduced pressure overnight, before use. The K10 clay (3 g) was added to an ethanolic solution (300 cm^3) of the complex C1 (0.3 mmol) and the resulting suspension was refluxed for 8 h. Then, the resulting material, labelled C1@K10, was filtered, washed with ethanol and dried in an oven for several hours.

Characterization methods

The Mn content was determined by atomic absorption spectroscopy (AAS) on a Pye Unicam SP9 spectrometer. X-ray diffractograms were obtained by the powder method, on a Philips PW 1710 diffractometer using CuK$_\alpha$ radiation and oriented mounts. Specific surface areas and pore volumes were obtained by the BET and *t*-method[11] respectively, from the nitrogen adsorption isotherms at −196 ºC determined with an automatic apparatus (Micromeritics, ASAP 2010). Before measurements, the samples were outgassed in vacuum at 150 ºC for 2.5 h.

X-ray photoelectron spectroscopy (XPS) was performed at the Centro de Materiais da Universidade do Porto (Portugal) on a VG Scientific ESCALAB 200A spectrometer, using non-monochromatised Al K$_\alpha$ radiation (1486.6 eV). To correct for possible deviations caused by the electric charge of the samples, the C 1s band at 285.0 eV was taken as internal standard. The materials were compressed into pellets prior to the XPS measurements. The XPS spectra were fitted using the XPSPEAK 4.1 program after a non-linear Shirley background subtraction. The atomic percentages were calculated from the corresponding peak areas, using the sensitivity factors provided by the manufacturer.

Catalytic experiments

The epoxidation of alkenes was studied at 0 ºC (ice bath) under constant stirring conditions. Briefly, 0.500 mmol of alkene, 0.500 mmol of chlorobenzene (GC internal standard) and 0.100 g of the heterogeneous catalyst were mixed in 5.00 cm^3 of solvent (dichloromethane or acetonitrile). Since the substrates show different reactivities towards the chosen oxidant systems, different experimental conditions were used. When *m*-chloroperoxybenzoic acid (*m*-CPBA) was used as oxidant, the compound *N*-methylmorpholine (NMO) was used as co-oxidant, and the proportion substrate/*m*-CPBA/NMO was 1:2:5. When iodosylbenzene was used as oxidant, the ratio substrate/oxidant was 2:1, and with sodium hypochlorite it was 2:3. In the latter case, the solution was buffered to pH 11 (Na_2HPO_4 + NaOH) to minimize the formation of chlorinated products.[12] During the experiments, 0.1 cm^3 aliquots were taken from solution with a hypodermic syringe, filtered through 0.2 μm syringe filters, and directly analysed by non-chiral and chiral GC-FID. At the end of each run, the catalysts were extracted/centrifuged sequentially three times with 10 cm^3 of methanol and three times with 10 cm^3 of dichloromethane, and then dried in an oven at 100 ºC overnight, before the new run or characterization.

The analysis of the products obtained after the catalytic experiments was done by GC-FID (using the internal standard method) on a Varian CP-3380 gas chromatograph equipped with 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), using helium as carrier gas. The epoxides enantiomeric excesses, in percentage (*ee*%), were determined with the same chromatograph, but using a fused silica Varian Chrompack capillary column CP-Chiralsil-Dex CB (25 m × 0.25 mm d.i. × 0.25 µm film thickness). Conditions used: 60 ºC (3 min), 5 ºC min^{-1}, 170 ºC (2 min), 20 ºC min^{-1}, 200 ºC (10 min); injector temperature, 200 ºC; detector temperature, 300 ºC.

The reaction parameters, such as %C (conversion, in percentage) and *ee*%, were calculated using the following formula, where A stands for the area of the chromatographic peak: $\%C = \{[A(alkene)/A(chlorobenzene)]_{t=0h} - [A(alkene)/A(chlorobenzene)]_{t=nh}\} \times 100/[A(alkene)/A(chlorobenzene)]_{t=0h}$ and $\%ee = [A(major\ enantiomer) - A(minor\ enantiomer)] \times 100/[A(major\ enantiomer) + A(minor\ enantiomer)]$. Epoxide selectivity: $\%S_{epoxide} = [A(alkene\ epoxide)] \times 100/[\sum A(each\ product)]$.

Results and Discussion

The X-ray diffractogram of an initial K10 sample (not shown) presented an expected peak corresponding to a basal spacing of 0.9 nm.[13] This diffraction peak was not detected in the various samples studied in Figure 1. However, for the K10 material with the immobilised complex (C1@K10), a broad peak at lower 2θ values was noticed. Further, Figure 1 suggests that the complex is intercalated between the clay layers, at least partially.

The presence of the complex was also confirmed by FTIR, Figure 2. The FTIR spectra are only presented in the 1800-1000 cm^{-1} range, since within this region the bands from the complex are not superimposed with the strong intensity bands of the unmodified K10 clay. In the FTIR spectrum of C1@K10, new peaks at 1540, 1440, 1420, 1390, 1340 and 1310 cm^{-1} can be observed, being associated with typical vibrations of the complex C1.

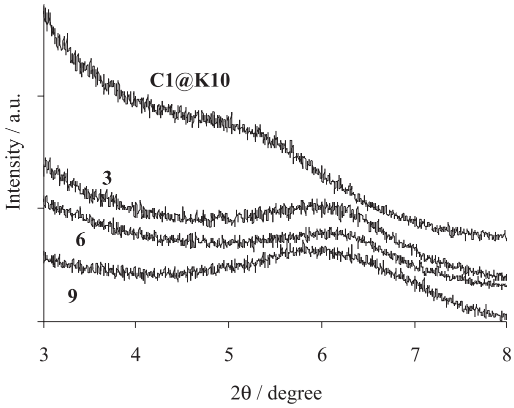


Figure 1. X-ray diffractograms for selected samples (see Table 1 for the labels).

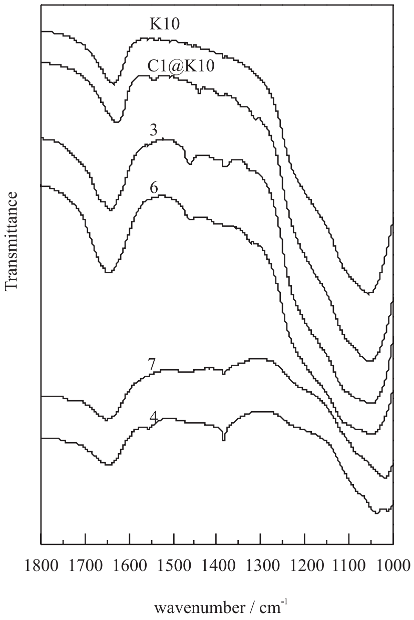


Figure 2. FTIR spectra for selected samples: K10, original C1@K10 and after catalytic reactions; the numbers refer to entries in Table 1.

The amount of loaded complex, determined by AAS (Table 1), is 31.4 µmol g^{-1}, corresponding to a complex immobilization efficiency of η = 31.4% (η(%) = amount of immobilized C1 × 100 / amount of C1 used in the material preparation). As can be disclosed from Figure 3a, the low temperature nitrogen adsorption-desorption isotherms for the K10 and the C1@K10 samples are essentially from a II + IV mixed type, according to the IUPAC classification.[14] This is an expected result, since K10 is a non-porous material, but still has some mesoporosity coming from the aggregation of crystallites, as denoted by the existence of the hysteresis loop. The K10 sample has a surface area of 223 m^2 g^{-1}, which is slightly reduced to 186 m^2 g^{-1} after the manganese complex immobilisation (Table 1). This small decrease is most probably a consequence of changes in the aggregation of the clay particles during the immobilisation procedure.

The surface chemical composition of the materials, determined by XPS (Table 2), confirms that the K10 clay is mainly composed of oxygen and silicon. Besides, it also contains small quantities of aluminium, magnesium, iron and potassium. The presence of small amounts of carbon and nitrogen can be due to the existence of organic impurities in the clay. The binding energies (BE) of the bands in the high resolution XPS spectra (Table 3) also provide information

Table 1. Specific surface areas, Mn contents and catalytic behaviour of the studied systems

Sample	Substrate	Oxidant system	Run	t[b] / h	C[c]	S[d]	*ee*[e]	A_{BET} / ($m^2 g^{-1}$)	Mn / (µmol g^{-1})
K10	---	---	---	---	---	---	---	223	---
C1@K10	---	---	---	---	---	---	---	186	31.4 (22[g])
1	styrene[a]	PhIO	1st	3	89[f]	58	7	146	8.8
2	styrene	*m*-CPBA/NMO	1st	<1	96	90	25		
	styrene	*m*-CPBA/NMO	2nd	3	24	72	11	129	29.2
3	styrene[a]	*m*-CPBA/NMO	1st	1	99	93	6		
	styrene[a]	*m*-CPBA/NMO	2nd	2	15	98	8	81	25.3
4	styrene	NaOCl	1st	48	25	51	14		
	styrene	NaOCl	2nd	72	2	100	15	7	8.8
5	α-Me-styrene[a]	PhIO	1st	3	85[f]	100	58		
	α-Me-styrene[a]	PhIO	2nd	<5	96[f]	86	64	166	6.4
6	α-Me-styrene	*m*-CPBA/NMO	1st	<1	100	98	39		
	α-Me-styrene	*m*-CPBA/NMO	2nd	2	49	97	18	84	5.7
7	α-Me-styrene	NaOCl	1st	3	16	38	16		
	α-Me-styrene	NaOCl	2nd	>72	6	100	30	12	9.6
8	6-CN-chromene	*m*-CPBA/NMO	1st	<1	62	95	79		
	6-CN-chromene	*m*-CPBA/NMO	2nd	3	37	100	10	149	12.7
9	6-CN-chromene	NaOCl	1st	<24	11	85	63	81	16.6
10	styrene	*m*-CPBA/NMO		<1	73	90	26		
11	styrene	NaOCl		>10	15	99	21		
12	6-CN-chromene	*m*-CPBA/NMO		<1	38	89	76		

Samples 1-9, heterogeneous systems (0.6% Mn/substrate); 10-12, homogeneous systems (0.5% Mn/substrate). [a]Solvent: acetonitrile (dichloromethane for all others); [b]reaction time; [c]conversion of substrate; [d]epoxide selectivity; [e]enantiomeric excess; [f]substrate conversion corrected for the limiting reactant PhIO; [g]determined by XPS.

about the clay structure. The high resolution XPS spectrum of the parent K10 shows a band in the O 1s region centred at 532.6 eV, associated with single bonded oxygen from the clay lattice, and a band at 103.3 eV in the Si 2p region, corresponding to silicon from the clay tetrahedral layers.[15] Similarly, there is a band at 74.9 eV, assigned to aluminium cations within the octahedral sheets.[13,16] The magnesium and iron cations present bands at 1303.9 eV and 712.8 eV respectively,[13,16] and the exchangeable potassium cations within the adjacent 2:1 layers show a characteristic band centred at 293.5 eV.

In the C1@K10 material, the presence of Mn in the clay composition, as well as the increase in the C and N surface contents, also confirm the manganese(III)-*salen* complex immobilisation within the clay. Additionally, the absence of K surface content can also be observed, suggesting that the complex was immobilised between the clay interlayers by ionic exchange with the potassium cations; there is also some decrease in the Mg, Al and Fe atomic percentages, probably due to structural reorganisation of the clay, as suggested by N_2 adsorption data.

In the high resolution XPS spectrum of C1@K10, the most relevant feature is the band centred at 642.0 eV in the Mn 2p region, which is characteristic of manganese(III) complexes with *salen* ligands,[17] indicating that the Mn oxidation number and the complex structure have been preserved after the immobilisation procedure.

Further insights about the complex location within the material are provided by comparison between the Mn surface and bulk contents determined by XPS and AAS respectively. The Mn surface loading is lower than the bulk one (Table 1), indicating that the complex is located inside the clay matrix, *i.e.*, in the interlayer region.

The catalytic behaviour of the immobilised complex, C1@K10 material, was studied in the enantioselective epoxidation of three alkenes, *viz.*: styrene, α-Me-styrene and 6-CN-chromene, using three different oxidant systems, according to the chemical reactions presented in Scheme 2. The catalytic results, specific surface areas and Mn contents after two runs are summarised in Table 1. In this table, the identification of the reactions catalysed by the immobilized C1 complex is also given: 1 to 4 reactions with styrene, 5 to 7 with α-Me-styrene and 8 and 9 with 6-CN-chromene.

The C1@K10 material was active in the catalytic epoxidation of the three alkenes, generally showing medium to high substrate conversions (C%), high epoxide selectivities (S%) and low to medium enantiomeric excesses (*ee*%), in the first run. All reactions using NaOCl as oxidant presented the lowest C%, whereas for S% no apparent correlation with the oxygen source or substrate was detected. The highest *ee*% values were obtained with α-Me-styrene and 6-CN-chromene, but no correlation can be established with the oxygen source.

After purification, the heterogeneous catalyst was used in another catalytic cycle, except for samples 1 and 9 (Table 1) due to the lack of material. Generally, for all the catalytic systems, the C1@K10 material showed a pronounced decrease in %C in the second cycle. In the majority of the cases, the %S values were slightly lower than in the first runs, except for samples 4 and 7 using NaOCl as oxidant, where significant %S increases were observed. Finally, the *ee*% also decreased, which is a common tendency observed for immobilized chiral catalysts.[2,3]

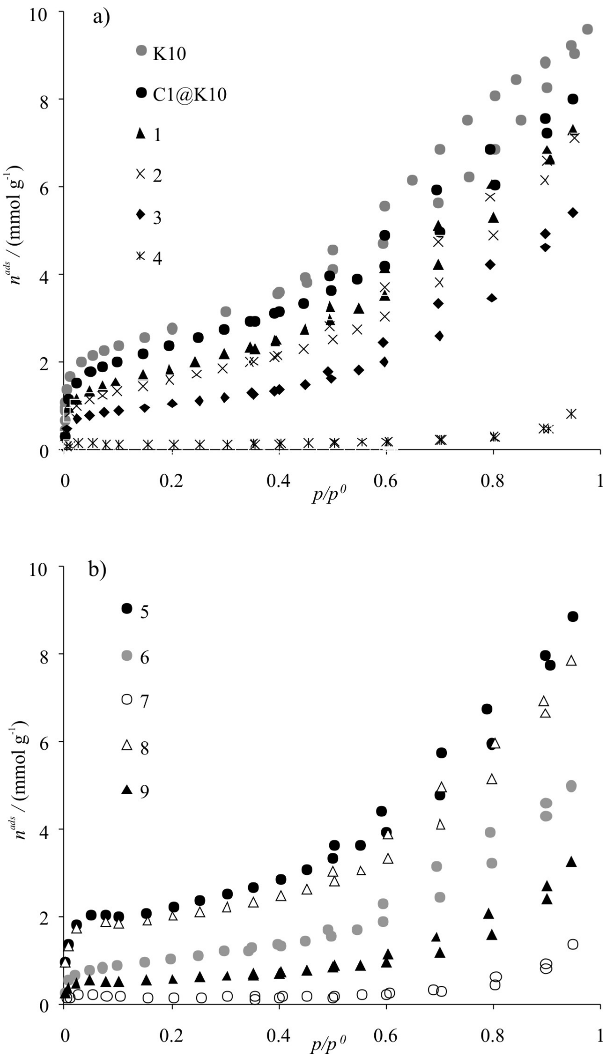
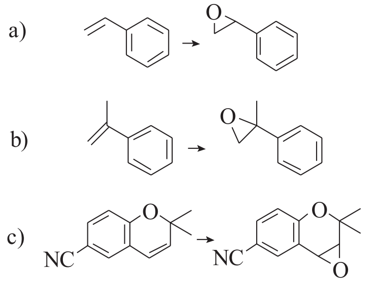


Figure 3. Nitrogen adsorption-desorption isotherms at −196 °C for the various samples: a) initial samples and after styrene catalysis; b) after α-Me-estyrene or 6-CN-chromene catalysis; the numbers refer to entries in Table 1.



Scheme 2. Epoxidation reactions of: a) styrene; b) α-Me-styrene; c) 6-CN-chromene.

Table 2. XPS surface chemical composition of the K10 based samples[a]

Sample	Atomic Percentage								
	C	N	O	Mg	Al	Si	K	Fe	Mn
K10	5.14	0.32	58.51	1.25	5.04	29.11	0.22	0.42	—
C1@K10	9.99	0.61	58.11	0.41	1.30	29.31	—	0.22	0.04

[a] Determined by the area of the respective XPS band in the high resolution spectra.

Table 3. Curve fitting data of the XPS spectra in the C 1s, O 1s, N 1s, F 1s, Mg 1s, Si 2p, Al 2p, Fe $2p_{3/2}$, K $2p_{3/2}$ and Mn $2p_{3/2}$ regions of the studied samples

Sample	Binding energy / eV[a]								
	C 1s	O 1s	N 1s	Mg 1s	Si 2p	Al 2p	Fe $2p_{3/2}$	K $2p_{3/2}$	Mn $2p_{3/2}$
K10	285.0 (2.6) 287.3 (3.0)	532.6 (2.6)	401.9 (5.4)	1303.9 (2.7)	103.3 (2.5)	74.9 (2.3)	712.8 (5.4)	293.5 (1.7)	—
C1@K10	285.0 (2.2) 286.8 (2.5)	533.2 (2.4)	400.6 (3.2)	1303.9 (2.6)	103.8 (2.3)	74.9 (2.1)	712.3 (5.8)	—	642.0 (4.6)

[a] Values between brackets refer to the full-width at half maximum of the bands.

To determine the causes of the progressive decrease in the performance of the catalyst upon reuse, the Mn bulk content was determined after the catalytic tests (Table 1) and the structural integrity of the material (in the different catalytic experimental conditions) was checked by XRD, FTIR and N_2 adsorption for some representative samples (Figures 1-3).

The differences between the Mn loadings before and after the catalytic reactions suggest that some complex leaching has occurred in all experimental conditions. This leaching occurred in different extents and with no correlation with the oxygen source used. In fact, when styrene was oxidized through *m*-CPBA/NMO (samples 2 and 3, Table 1), a complex leaching of less than 20% was observed, whereas values higher than 50% were obtained in other cases (entries 4-7, Table 1). Although complex leaching was observed for all studied reactions, there is no direct relationship between the %C decrease upon reuse and the Mn content after the two catalytic cycles. This observation may suggest that the decrease in %C is determined not only by complex leaching, but also by some metal complex deactivation and/or decomposition during the catalytic cycles or, ultimately, by some clay structural disruption.

Figure 1 reflects the main features observed after catalytic reuse: for all samples used in the epoxidation of alkenes (one sample for each alkene, 3, 6 and 9), the broad diffraction peak, which was attributed above to the insertion of the complex between the clay layers, is now shifted for higher 2θ values, indicating a decrease in the basal spacing. Therefore, these results confirm the complex leaching from the clay interlayers. Furthermore, the FTIR spectra of selected samples recorded after reuse (Figure 2, samples 3, 4, 6, 7), showed band broadening in the 1620-1200 cm^{-1} region, which corresponds to the frequency range where bands due to the complex occur, also suggesting complex leaching and eventually some complex degradation. When NaOCl was used as oxidant, changes in the bands related with the K10 matrix could also be detected after the catalytic reactions; herein, it must be mentioned that the oxidation of alkenes using NaOCl as oxygen source requires pH 11 to prevent the formation of chlorinated products. Therefore, these results suggest that the high pH value induces some structural changes in the K10 support itself.

The N_2 adsorption isotherms of the samples after catalysis (Figure 3) can also provide some insights regarding the stability/integrity of the reused materials. After the styrene epoxidation reactions (samples 1 to 4), the nitrogen adsorbed amounts (Figure 3a) were successively reduced as the oxidant was changed from PhIO to the *m*-CPBA/NMO system, achieving the lowest value when NaOCl was used as oxygen source; a similar pattern was observed for the other two substrates used. These facts suggest that, concomitantly to the catalytic reaction, there are significant changes within the structure/external organization of the clay support, which are greater in the epoxidation reaction that uses NaOCl as oxygen source. Moreover, these changes probably induce the observed catalyst deactivation or leaching of the immobilised complex.

Conclusions

The K10-montmorillonite clay was used as a support for the immobilisation of a cationic derivative of Jacobsen catalyst. This new heterogenised catalyst was active in the enantioselective epoxidation of styrene, α-Me-styrene and 6-CN-chromene, using three different oxidant systems. The results obtained using NaOCl were the most unfavourable ones of the series, independently of the alkene used. Apparently, this oxidant system may cause a severe disruption of the heterogeneous catalyst. In general, in all cases good selectivities for the epoxide products were observed, whereas the highest enantiomeric excess values were obtained for α-Me-styrene and 6-CN-chromene. Some leaching of the active phase occurred for all systems after the catalytic runs. At this point it is not entirely clear whether the main reasons for the complex leaching, and consequent activity loss, are the lack of strong interactions between the clay and the complex, or the decomposition of the complex with disruption of the clay structure, both induced by the strong oxidant systems usually employed in this type of reactions.

In this way, the use of clays, such as the K10 montmorillonite, as supports for the immobilization of catalytic active epoxidation complexes should continue to be pursued, since additional progress is needed to achieve a deeper knowledge of the influence of the oxidant systems in the catalysts integrity. The search and optimization of less aggressive oxidant systems, not only for the complexes but also for the supports, are also desirable.

Acknowledgments

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