Styrene oxidation by manganese Schiff base complexes in zeolite structures

M. Silva [a], C. Freire [b], B. de Castro [b], J.L. Figueiredo [a,*]

[a] *Laboratório de Catálise e Materiais, Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto,
Rua Dr. Roberto Frias, 4200-465 Porto, Portugal*
[b] *REQUIMTE, Departamento de Química, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, 4169-007 Porto, Portugal*

Abstract

Styrene oxidation was investigated using manganese(III) *salen* complexes as catalysts in homogeneous media and encapsulated in NaX and NaY zeolites using *tert*-butylhydroperoxide as the oxygen source. The oxidation of styrene led to formation of benzaldehyde, styrene oxide and phenylacetaldehyde, with minor amounts of phenyl-1,2-ethane-diol; some polymer formation was also observed. In homogeneous media, both complexes with ligands functionalized with methoxyl groups showed similar styrene conversions and chemoselectivities in styrene epoxide and benzaldehyde. Upon immobilization, [Mn(3-MeOsalen)]@X showed the highest catalytic activity at 60 °C and atmospheric pressure, and the highest chemoselectivities in styrene epoxide and benzaldehyde. No leaching of the encapsulated metal complexes was observed during the catalytic reactions and support for the entrapment of metal complexes inside the zeolite cages and not on their external surfaces was provided by nitrogen adsorption analyses and SEM micrographs.

The reaction mechanism was investigated using the most active heterogeneous catalyst, [Mn(3-MeOsalen)]@X, and the influence of various reaction parameters, such as substrate, catalyst concentration and temperature, on alkene conversion and styrene epoxide yield have been studied. Furthermore, the homogeneous oxidation of styrene using [Mn(3-MeOsalen)CH$_3$COO] was monitored by electronic spectroscopy, the results suggesting a free radical mechanism involving a peroxomanganese species as the catalyst active intermediate.
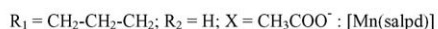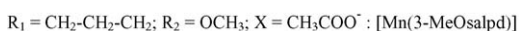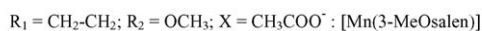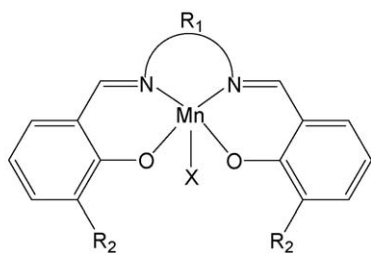© 2006 Elsevier B.V. All rights reserved.

Keywords: Styrene oxidation; Mn(III) *salen* complexes; Zeolites; Metal complex encapsulation

1. Introduction

The use of metal complexes immobilized into solid supports as heterogeneous catalysts has become very important for ecofriendly industrial processes. These materials have been developed with the objective to perform reactions under milder conditions and without hazardous wastes. These new catalysts can easily be separated from the reaction media and reused, as they are quite stable when compared with the corresponding homogeneous counterparts, since catalyst deactivation pathways are hindered by local site isolation of the complexes inside the solid matrix. Among a variety of supports, zeolites have been often used; this new generation of immobilized catalysts has been named "zeolite encapsulated metal complexes" (ZEMC) [1].

Transition metal Schiff base complexes are active homogeneous catalysts in oxidation reactions of organic substrates. One of the most important oxidation reactions is the oxidation of alkenes [2–4], and manganese(III) complexes with *salen* type ligands have been shown to be highly effective, chemoselective and stereoselective for this reaction, and when chiral ligands are used, they can also be highly enantioselective [5–7]. Several oxygen donors have been used for the oxidation of alkenes via manganese(III) *salen* complexes, such as iodosylbenzene, 3-chloroperoxybenzoic acid, sodium hypochlorite, dioxygen, hydrogen peroxide and *tert*-butylhydroperoxide [5,8,9]. The catalytic active intermediates, the steps involved in the catalytic cycle, and thus the type of oxidation products, are a matter of strong debate [10–12] since they strongly depend on the oxygen donor, solvent (reaction media conditions, presence of co-catalyst) and the metal complex, specifically the ligand, through the different steric and electronic properties of its substituents. Most of the mechanistic studies are related to homogeneous phase [10–12] and only a few examples focus on reactions catalyzed by heterogenized metal complexes [13–15].

---

* Corresponding author. Tel.: +351 225081663; fax: +351 225081449.
E-mail address: jlfig@fe.up.pt (J.L. Figueiredo).

R$_1$ = CH$_2$-CH$_2$; R$_2$ = OCH$_3$; X = CH$_3$COO$^-$: [Mn(3-MeOsalen)]

R$_1$ = CH$_2$-CH$_2$-CH$_2$; R$_2$ = OCH$_3$; X = CH$_3$COO$^-$: [Mn(3-MeOsalpd)]

R$_1$ = CH$_2$-CH$_2$-CH$_2$; R$_2$ = H; X = CH$_3$COO$^-$: [Mn(salpd)]

Scheme 1. Molecular structure of manganese(III) *salen* complexes.

We have been interested in the immobilization of nickel, copper and manganese *salen* complexes in several supports, such as activated carbons [16–18], pillared clays [19] and zeolites [20,21], with the final goal of preparing high chemoselective, stable and recyclable heterogeneous catalysts for oxidation reactions. Several strategies have been developed for the immobilization of the complexes onto the different supports, but the final proof for the catalysts chemoselectivity and stability (efficient immobilization with the same conformation of the neat complex) is their test in the catalytic reactions.

In this work we describe the oxidation of styrene (one of the most important pro-chiral alkenes) in the presence of the ecofriendly oxidant *tert*-butylhydroperoxide (*t*-BuOOH), using three manganese(III) *salen* complexes as catalysts – Scheme 1 – both in homogeneous medium and encapsulated in NaX and NaY zeolites; the latter catalysts being denoted as [Mn(salen)]@X or Y. The reaction mechanism was investigated with the most active heterogeneous catalyst, [Mn(3-MeOsalen)]@X, and the influence of various reaction parameters, such as substrate and catalyst concentration and temperature, on conversion and yield has been studied.

2. Experimental

2.1. Materials

2-Hydroxybenzaldehyde, 3-methoxy-2-hydroxybenzaldehyde, ethylenediamine and propylenediamine were purchased from Merck; manganese(II) acetate tetrahydrate, acetonitrile (99.9%), dichloromethane (99.6%), phenylacetaldehyde (90+%), phenyl-1,2-ethane-diol (97%) and acetophenone (99%) were purchased from Aldrich and styrene (99.5%), benzaldehyde (99+%), styrene oxide (97%), *n*-decane (99%) and *tert*-butylhydroperoxide (70% solution in water) were originated from Fluka. NaX and NaY were supplied by Grace GmbH.

2.2. Preparation of ligands and complexes

The ligands H$_2$salen (bis-salicylaldehyde-ethylenediimine), H$_2$salpd (bis-salicylaldehyde-propylenediimine), H$_2$(3-MeO-

salen) (bis-(3-methoxy)salicylaldehyde-ethylenediimine) and H$_2$(3-MeOsalpd) (bis-(3-methoxy)salicylaldehyde-propylenediimine) were synthesized by a standard procedure [22–24], by refluxing 2-hydroxybenzaldehyde and its derivative 3-methoxy-2-hydroxybenzaldehyde with ethylenediamine or propylenediamine in ethanolic solution. The respective manganese(III) complexes (Scheme 1) were prepared by a procedure described in the literature [22–24], by reaction of the ligands with manganese(II) acetate tetrahydrate in ethanol. The characterization of the complexes will be described in detail elsewhere. The most relevant IR bands are summarized as follows:

[H$_2$(3-MeOsalen)] (v, cm^{-1}): 3000(sh), 2939(b), 2848(b), 1633(s), 1471(s), 1410(sh), 1259(s), 1089(m). [H$_2$(3-MeOsalpd)] (v, cm^{-1}): 3050(sh), 2939(b), 1634(s), 1472(s), 1382(sh), 1264(s), 1090(m). [H$_2$(salpd)] (v, cm^{-1}): 3010(sh), 2882(b), 1631(s), 1287(m), 1207(m). [Mn(3-MeO)salen] (v, cm^{-1}): 3018(sh), 2922(s), 2861(sh), 1585(m), 1471(m), 1411(sh). [Mn(3-MeO)salpd] (v, cm^{-1}): 3052(w), 2922(w), 2861(w), 1613(b), 1445(b), 1328(sh), 1231(m), 1076(m).

2.3. Preparation of exchanged zeolites

Mn(II)@X and Mn(II)@Y were prepared by dissolving manganese(II) acetate tetrahydrate in deionized water to which NaX or NaY were added; the mixture was in stirring for 24 h. The solid products were then filtered and washed thoroughly with warm water. The light pink solids were dried at 150 °C.

2.4. Preparation of encapsulated complexes by the flexible ligand method

Intrazeolite metal complexes [Mn(salen)]@X or [Mn(salen)]@Y (the anion CH$_3$COO$^-$ was omitted for clarity) were prepared by the flexible ligand method [25]: the exchanged Mn(II) zeolites were mixed with the prepared Schiff base ligands and heated for several hours. During this reaction the ligand complexed the exchanged Mn(II) cations and there is simultaneously the oxidation of the metal centre to Mn(III), leading to a colour change to dark brown-greenish, typical of Mn(III) *salen* complexes. The resulting materials were Soxhlet extracted sequentially with dichloromethane, acetonitrile and ethanol for a total period of time of 48 h. The solids were then dried for several hours. The characterization of the materials will be described in another paper. The most relevant IR bands are summarized as follows:

[Mn(salpd)@X] (v, cm^{-1}): 3504(b), 3255(sh), 1643(s), 1390(w). [Mn(salpd)@Y] (v, cm^{-1}): 3560(b), 3487(sh), 1635(s). [Mn(3-MeO)salpd@X] (v, cm^{-1}): 3490(b), 1635(s), 1397(w). [Mn(3-MeO)salpd@Y] (v, cm^{-1}): 3556(b), 3471(sh), 1635(s). [Mn(3-MeO)salen@X] (v, cm^{-1}): 3463(b), 1635(s), 1397(w). [Mn(3-MeO)salen@Y] (v, cm^{-1}): 3510(b), 1635(s).

2.5. Catalyst characterization

The manganese contents of the modified zeolites were evaluated by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) at Kingston Analytical Services, UK.

X-ray powder diffraction (XRD) patterns of the materials were obtained at Universidade de Aveiro, Portugal. Scanning electron microscopy (SEM) was performed at Centro de Materiais da Universidade do Porto, Portugal. Nitrogen adsorption measurements were done in a Coulter Omnisorp 100CX analyzer. The samples were previously degassed at $150\,^{\circ}C$ to a vacuum of 10^{-3} Pa; the adsorption of nitrogen was carried out at $-196\,^{\circ}C$. The electronic spectra of the neat complexes were taken on a JASCO V-560 spectrophotometer (double monochromator). The IR spectra of the complexes and materials were recorded in KBr pellets, using a Nicolet 510P spectrophotometer with a diffuse reflectance cell, in the range 400–$4000\,cm^{-1}$.

2.6. Catalytic activity

The styrene oxidation reactions were carried out in a batch glass reactor of 10 ml volume, under atmospheric pressure. The reactor was equipped with a reflux condenser. In a typical experiment, 2.0 mmol of styrene and 2.0 mmol of *n*-decane were mixed with 3 ml of dichloromethane, and then 0.1 g (zeolites with encapsulated complexes) or 0.05 g (free complexes) of the catalyst was introduced in the reactor. After increasing the temperature of the mixture to $60\,^{\circ}C$, 2.0 mmol of *t*-BuOOH were added. The reaction was carried out for 10 h. Aliquots were withdrawn at fixed time intervals (1 h) and analyzed by GC (Dani 1000, with a DB Waxetr column), with a FID detector. The normalized amounts of styrene converted and the normalized yields of the oxidation products were estimated by the internal standard method (*n*-decane). Identification of these products was confirmed by GC–MS (VARIAN CP-3800, with a Chrompack DB-1 column). For kinetic studies, different substrate, oxidant and catalyst concentrations were used

3. Results and discussion

The ligands and the complexes show typical IR vibrations [22–24] due to the ν C–H bond in the range 3000–$2800\,cm^{-1}$ (from the C–H in the imine bridge), the ν C=N and C=C (due to the imine bond formed through Schiff condensation of the diamines with the aldehydes, and C=C from the aldehyde moiety) in the range 1650–$1450\,cm^{-1}$ and ν C–O within 1300–$1100\,cm^{-1}$. After encapsulation of the complexes by the in situ synthesis, the IR spectra of the materials show, superimposed on the strong bands due to the zeolite matrix, some low intense bands that are assigned to the complexes, namely the ν C–H and ν C=N and C=C vibrations, indicating that the complexes have been formed inside the zeolite cavities.

3.1. Morphological and textural properties of the heterogeneous catalysts

The manganese contents of the modified zeolites are summarized in Table 1; the %Mn values are in the range 0.5–1% wt. Upon in situ synthesis of the Mn complexes in the zeolites there is a decrease in the Mn content, suggesting that during complex encapsulation there is some Mn leaching. This decrease is higher for complex encapsulation in zeolite Y, suggesting that

Table 1
Micropore volume and mesopore surface area for the prepared catalysts and manganese percentage

Catalyst	Micropore volume[a], V_{mic} (cm^3 g^{-1})	S_{meso}[a] (m^2 g^{-1})	Mn[b] (%)
NaX	0.28	92	
NaY	0.29	87	
Mn@X	0.26	89	1.0
Mn@Y	0.29	68	0.99
[Mn(3-MeOsalen)]@X	0.24	86	0.80
[Mn(3-MeOsalen)]@Y	0.29	68	0.76
[Mn(3-MeOsalpd)]@X	0.25	75	0.76
[Mn(3-MeOsalpd)]@Y	0.27	72	0.58
[Mn(salpd)]@X	0.24	78	0.86
[Mn(salpd)]@Y	0.28	63	0.51

[a] From *t*-plot.
[b] Determined by ICP-AES.

it can be associated with some hydrolysis of the imine bond of the as-formed complexes (resulting in the decomposition of the complexes), induced by the higher acidity of this zeolite, thus leading to lower immobilisation yield for the complexes in zeolite Y, when compared to zeolite X.

The X-ray powder diffractograms of all materials indicate a well crystalline FAU structure of cubic symmetry [26]; they did not reveal any significant difference from those of parent materials as all the characteristic peaks are present and their widths at half height are unchanged. Only a small decrease is observed in the intensities of the peaks at $2\theta < 20^{\circ}$, which is a consequence of the redistribution of the ions in the exchanged zeolites. This suggests that the overall integrity of the framework of the zeolite has been preserved upon the encapsulation of manganese complexes [27]; some of the XRD patterns of the synthesized samples of zeolite NaX are shown in Fig. S1. SEM micrographs of the modified zeolites (Fig. S2) show irregular 1–2 µm cubic particles similarly to the parent materials, also indicating that upon complex entrapment the crystallinity of the parent zeolites was kept.

The nitrogen adsorption isotherms for the parent (NaX and NaY) and the modified zeolites are typical of microporous materials [28]; however, the micropore volumes and the mesopore surface areas of the modified zeolites (Table 1) show a decrease when compared with the parent materials, which is a consequence of the presence of metal–*salen* complexes within the cavities [27], as the external cationic exchange sites are only 1% [29]; similar observations can be found for phthalocyanine complexes [29] and other *salen* type complexes [30]. In NaX zeolite the observed reduction is in the range 7 and 14%, whereas in NaY zeolites the decrease varies from 0 to 7%, when compared with the respective parent zeolites. The difference in these values can be a consequence of the different material acidity which result in different complexation processes.

3.2. Catalytic activity

The catalysts (metal complexes and modified zeolites) were used in the oxidation of styrene (an electron rich olefin) using *tert*-butylhydroperoxide (*t*-BuOOH) as the oxidant and

Table 2
Catalytic epoxidation of styrene with neat and zeolite encapsulated complexes

	Normalized amounts converted	Normalized yields			
		SO	BA	PA	PD
Neat complex[a]					
[Mn(3-MeOsalen)]CH$_3$COO	5.6	2.4	3.5	0.0053	0
[Mn(3-MeOsalpd)]CH$_3$COO	6.0	2.7	3.1	0.0036	0
[Mn(salpd)]CH$_3$COO	3.8	0.51	3.3	0.0012	0
Zeolites with encapsulated complex[b]					
Mn@X	11	0.99	6.0	3.8	0
[Mn(3-MeOsalen)]@X	18	4.9	6.6	5.2	2.4
[Mn(3s-MeOsalpd)]@X	13	2.2	2.0	6.1	0
[Mn(salpd)]@X	8.6	0.18	3.4	4.5	0.51
Mn@Y	10	1.5	5.4	3.3	0.016
[Mn(3-MeOsalen)]@Y	17	3.1	2.4	5.7	0.79
[Mn(3-MeOsalpd)]@Y	8.7	2.1	4.5	2.3	0
[Mn(salpd)]@Y	7.4	0.022	4.1	2.8	0.38

SO, styrene oxide; BA, benzaldehyde; PA, phenylacetaldehyde; PD, phenyl-1,2-ethane-diol.

[a] Amounts converted after 6 h of reaction time per mole of Mn.
[b] Amounts converted after 8 h of reaction time per mole of Mn.

dichloromethane as the solvent, at 60 °C. The results are compiled in Table 2 and in Figs. 1–3 are depicted the normalized amounts converted and the normalized yields as a function of reaction time; these parameters are defined, respectively, as: $n^0_{sty} X_{sty}/n_{Mn}$ and $n_{product}/n_{Mn}$, where X_{sty} is the styrene conversion, n^0_{sty} the initial amount of styrene, $n_{product}$ the amount of product, and n_{Mn} the amount of Mn in the catalyst.

The experimental results show that all the complexes are active in the homogeneous oxidation of styrene, with benzaldehyde (BA) as the major oxidation products, followed by stryrene oxide (SO), similarly to literature [31,32]; some polymer formation was also observed.

The normalized amounts converted and epoxide normalized yield are higher for the complexes functionalized with the methoxyl group in the aldehyde moiety. This increase cannot be assigned only to an electronic tuning of the catalyst performance, as there are some small differences in the solubility of complexes in the reaction medium, which influence the rate of their catalytic reaction: the complexes functionalized with methoxyl groups show similar solubility [Mn(3-MeOsalpd)]CH$_3$COO ~ [Mn(3-MeOsalen)]CH$_3$COO which is higher than that of the non-functionalised complex [Mn(salpd)]CH$_3$COO. Nevertheless, at the end of the first catalytic cycle there is a change in the colour of the solution from light brown to dark brown, suggesting the decomposition of the molecular catalysts.

Upon encapsulation the complexes are still active in the oxidation of styrene (Figs. 2 and 3) with product distributions similar to the homogeneous reactions, except for the presence of phenylacetaldehyde (C) (Scheme 2), formed via ring opening of phenyloxirane on acid sites of the zeolites [32], and phenyl-1,2-ethane-diol.

Among the heterogeneous catalysts, those based in zeolite X have higher conversions and styrene oxide normalized yields, the material [Mn(3-MeOsalen)]@X being the most active catalyst. The latter result can be a consequence of the higher acidity of
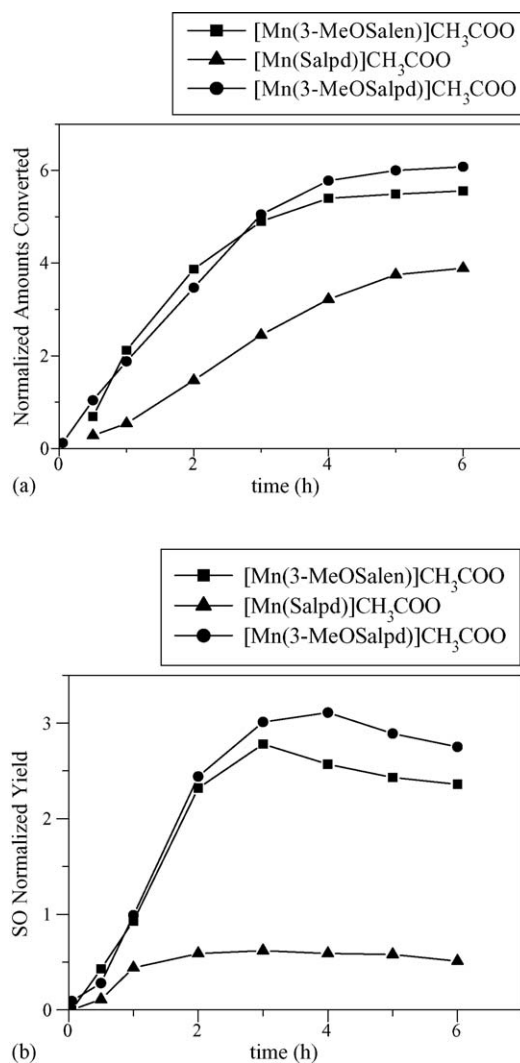

Fig. 1. (a) Styrene normalized conversion and (b) normalized yields in styrene oxide with the free complexes.

the zeolite Y, when compared with zeolite X, which will induce epoxide ring opening.

The heterogeneous catalytic activity follows the trend: [Mn(3-MeOsalen)]@X > [Mn(3-MeOsalpd)]@X > [Mn(salpd)]@X; a similar trend is observed for the NaY based zeolites. As in homogeneous phase, the complexes functionalized with methoxyl groups have higher catalytic activity than the non-functionalised complex, [Mn(salpd)]. Nevertheless, for the functionalized complexes, that with the smaller imine bridge, [Mn(3-MeOsalen)], has higher catalytic activity.

At the end of the first catalytic cycle, there was no colour change of the solution or catalysts, suggesting that no decomposition of the complexes took place during the reaction. The materials were easily separated from the reaction medium, and the observation that no further styrene conversion occurred upon removal of the heterogeneous catalyst from the reaction medium subsequent to 3 h of reaction indicates that styrene oxidation is catalyzed essentially by the encapsulated metal complexes, and that no leaching of the active species have occurred during the catalytic cycle.
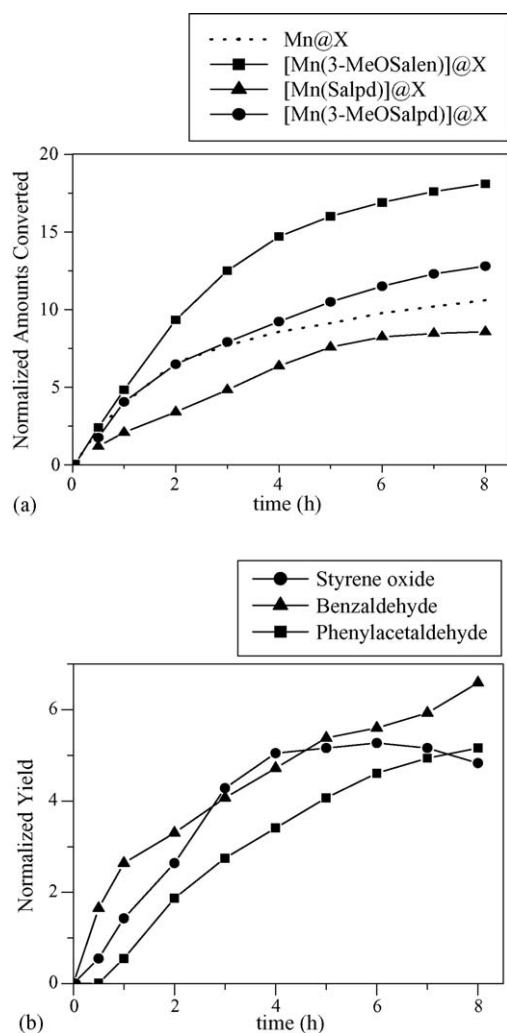
Fig. 2. (a) Styrene normalized conversion with the modified zeolite X and (b) normalized yields in benzaldehyde, styrene oxide and phenylacetaldehyde of the [Mn(3-MeOSalen)]@X.
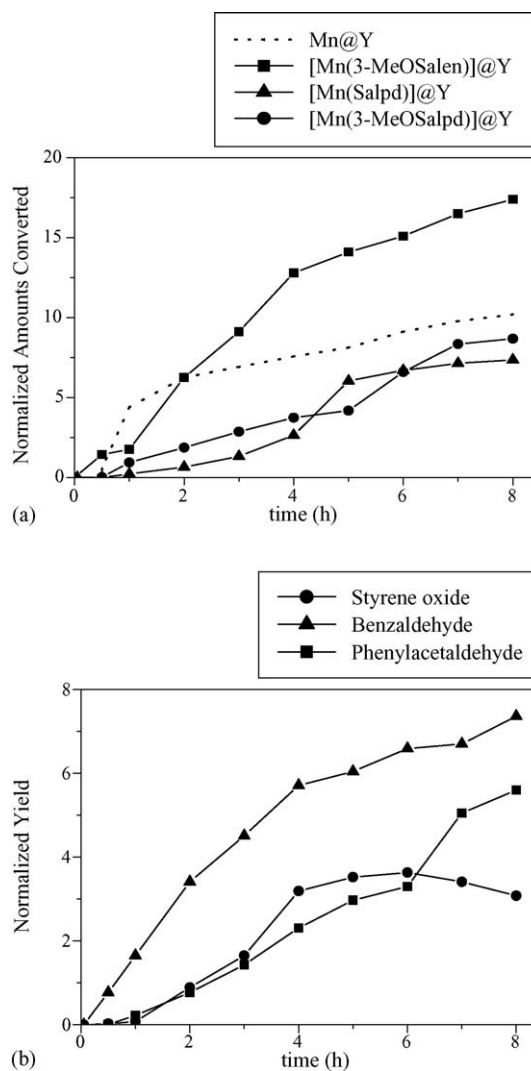

Fig. 3. (a) Styrene normalized conversion with the modified zeolite Y and (b) normalized yields in benzaldehyde, styrene oxide and phenylacetaldehyde of the [Mn(3-MeOSalen)]@Y.

Styrene oxidation in homogeneous medium was studied by electronic spectroscopy, using the complex [Mn(3-MeOsalen)]CH$_3$COO in dichloromethane. When t-BuOOH was added to the reaction mixture the band maximum due to the complex, initially at $\lambda = 410$ nm, shifted to $\lambda = 430$ nm, confirming the formation of a metal-based catalytic active intermediate (Fig. 4), as reported in literature [33,34]. The intermediate species is a metalloxo manganese complex with high-valence (Mn(V)=O) [14,15,32]; this active intermediate is generally favoured with early transition metals (Mo(VI), W(VI) and V(V)) and many first row transition metals, including manganese, follow such metal oxo-catalysed route. The intensity of this band increases as a consequence of products formation and the t-BuOOH decomposition.

The mechanism for the oxidation of styrene via a Mn(V)=O intermediate, when using t-BuOOH, usually involves two pathways with different t-BuOOH molecularity [34,35]. The proposed mechanism for the catalytic reaction studied in this work with the homogeneous catalyst is described in Scheme 3: (i) a radical chain reaction (one electron transferred), leading to

benzaldehyde, in which the t-BuOOH molecularity is 2; (ii) an oxidation reaction (two electrons transferred), leading to styrene oxide, with t-BuOOH molecularity equal to 1. The oxygen transfer from species (d) to species (e) is the limiting step. The role of CH$_2$Cl$_2$ in the mechanism was not evaluated. Taking into consideration that the concentration of species (d) is much lower than that of species (a) (Scheme 3), the following rate law can
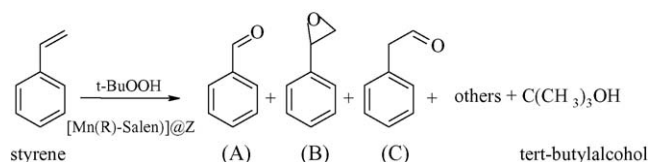
Scheme 2. Products of the catalytic oxidation of styrene in the presence of the encapsulated complexes: (A) benzaldehyde; (B) styrene oxide; (C) phenylacetaldehyde. The term "others" includes phenyl-1,2-ethane-diol and polymeric products of low molecular weight. The mass balance deficiency is the result of acetophenone and the polymeric products.
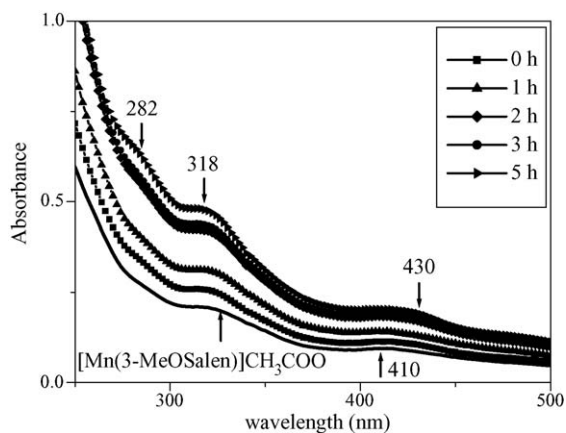
Fig. 4. Electronic spectra for the homogeneous oxidation of styrene by [Mn(3-MeOsalen) CH$_3$COO], taken at increasing reaction times. The spectrum of the catalyst in solution is given for reference.

be obtained for the production of styrene oxide:

$$\text{rate} = \frac{k_4 K_1 K_3 [\text{Sty}][\text{catalyst}]_T \{[C(CH_3)_3OOH]/[C(CH_3)_3OH]\}}{1 + K_1 \{[C(CH_3)_3OOH]/[C(CH_3)_3OH]\}}$$

where k_4 is the rate constant, K_1 and K_3 equilibrium constants, and [X] is the concentration of compound X.

Kinetic studies were performed with the heterogeneous catalyst [Mn(3-MeOsalen)]@X, as it was the most active catalyst in the oxidation reaction. The kinetics of the oxidation of styrene

Scheme 3. Proposed mechanism for oxidation of styrene with manganese *salen* complexes in the presence of *t*-BuOOH.

Table 3
Epoxidation of styrene by [Mn(3-MeOsalen)]@X under different reaction conditions

|	n_{cat} (mmol)	n_{Sty} (mol)	$n_{t\text{-BuOOH}}$ (mol)	T (°C)	$r \times 10^3$ (mol h^{-1} g^{-1})
Catalyst effect					
1	0.022	0.0020	0.0020	60	7.11
2	0.015	0.0020	0.0020	60	4.95
3	0.007	0.0020	0.0020	60	2.16
4	0.003	0.0020	0.0020	60	0.858
Substrate effect					
1	0.010	0.0040	0.0020	60	9.54
2	0.010	0.0020	0.0020	60	5.52
3	0.010	0.0010	0.0020	60	2.36
4	0.010	0.0005	0.0020	60	1.17
tert-Butylhydroperoxide effect					
1	0.010	0.0020	0.0080	60	11.1
2	0.010	0.0020	0.0040	60	8.21
3	0.010	0.0020	0.0020	60	5.52
4	0.010	0.0020	0.0015	60	4.56
Temperature effect					
1	0.010	0.0020	0.0020	40	1.23
2	0.010	0.0020	0.0020	50	2.56
3	0.010	0.0020	0.0020	60	5.52
4	0.010	0.0020	0.0020	70	10.2

catalyzed by [Mn(3-MeOsalen)]@X were investigated by varying the concentrations of catalyst, substrate and oxidant, and temperature, and the results are summarised in Table 3.

The rates of oxidation of styrene, in all the experiments, were evaluated graphically from the amount of styrene converted as function of time. From the data presented in Table 3, first order with respect to both the substrate and the catalyst is suggested, but a reaction order of 1/2 is found with respect to the oxidant. These results are in good agreement with the rate law deduced for homogeneous phase reaction, since a first order dependency was observed with respect to [Sty] and [catalyst]$_T$, whereas the reaction order with respect to [*t*-BuOOH] is fractionary. In this context, we can conclude that the same reaction mechanism must occur in heterogeneous phase. Further confirmation for the proposed mechanism can be gathered from the experiments where the oxidant quantity was varied. In fact, because in the proposed mechanism there are two paths that have different *t*-BuOOH molecularity that leads to different products (benzaldehyde and styrene epoxide) it would be expected that the variation of the oxidant concentration in the reaction medium would lead to different chemoselectivity: in the present case, an increase in the concentration of the oxidant should lead to a decrease in the styrene oxide selectivity. Table 4 summarizes the

Table 4
SO normalized yield as a function of the oxidant number of moles

Experiment	$n_{t\text{-BuOOH}}$ (mol)	SO normalised yield
1	0.0080	2.0
2	0.0040	3.5
3	0.0020	4.9
4	0.0015	6.0
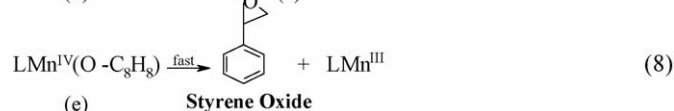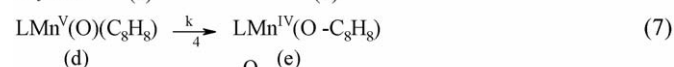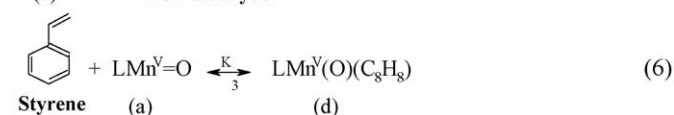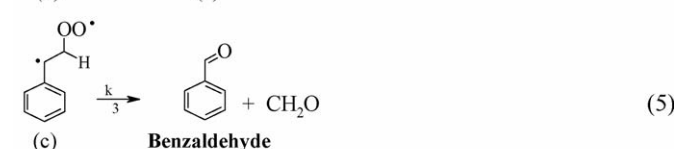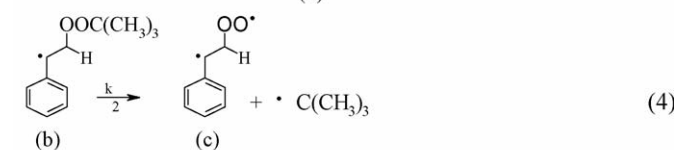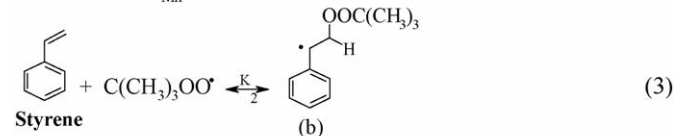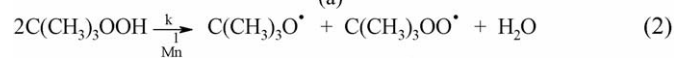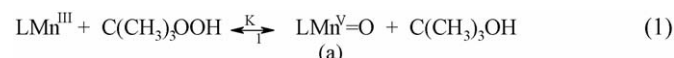
styrene oxide normalised yields as a function of the *t*-BuOOH quantity used in the catalytic reaction. Analysis of the data confirms the expected results based in the proposed mechanism: the increase in *t*-BuOOH quantity favours the radical chain reaction, leading to benzaldehyde and thus decreasing the styrene oxide. The key conclusion to be drawn from this study is that when using Mn(III)*salen* catalysts coupled to *t*-BuOOH as the oxygen source in the oxidation of alkenes, the chemoselectivity of the epoxide is improved when the content of *t*-BuOOH in the reaction medium is kept in deficit with respect to the catalyst content.

4. Conclusions

Salen complexes of manganese(III) were encapsulated in the supercages of zeolites X and Y by the flexible ligand method with preservation of the zeolite cristallinity and morphology.

Both neat and encapsulated manganese(III) complexes were active in the oxidation of styrene using *t*-BuOOH as the oxygen source under mild conditions and the catalytic activity pattern did not change upon encapsulation: the major product was benzaldehyde, followed by styrene epoxide.

Electronic spectroscopy was used to probe the mechanism of styrene oxidation in homogeneous media using the complex [Mn(3-MeOsalen)]CH$_3$COO in dichloromethane. The results suggest a mechanism via a Mn(V)=O intermediate, involving two pathways with different *t*-BuOOH molecularity: a radical chain reaction which originates mainly benzaldehyde and an oxidation reaction leading to styrene oxide; the respective rate law was deduced.

The kinetics of the heterogeneous oxidation of styrene catalyzed by [Mn(3-MeOsalen)]@X were investigated by varying the concentrations of catalyst, substrate and oxidant, and temperature. The results were in agreement with the rate law deduced for the homogeneous reaction, suggesting that the same mechanism of the homogeneous phase catalytic reaction is operative upon encapsulation of the complexes.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2006.05.070.

References

[1] T. Joseph, D.P. Sawant, C.S. Gopinath, S.B. Halligudi, J. Mol. Catal. A: Chem. 184 (2002) 289.
[2] E.G. Samsel, K. Srinivasan, J.K. Kochi, J. Am. Chem. Soc. 107 (1985) 7606.
[3] M.J. Upadhyay, P.K. Bhattacharya, P.A. Ganeshpure, S. Satish, J. Mol. Catal. 73 (1992) 277.
[4] K. Srinivasan, P. Michaud, J.K. Kochi, J. Am. Chem. Soc. 108 (1986) 2309.
[5] T. Katsuki, Coord. Chem. Rev. 140 (1995) 189.
[6] W. Zhang, J.L. Loebach, S.R. Wilson, E.N. Jacobsen, J. Am. Chem. Soc. 112 (1990) 2801.
[7] M.J. Sabater, A. Corma, A. Domenech, V. Fornés, H. Garcia, Chem. Commun. (1997) 1285.
[8] T. Katsuki, J. Mol. Catal. A: Chem. 113 (1996) 87.
[9] D.E. De Vos, P.P. Knops-Gerrits, D.L. Vanoppen, P.A. Jacobs, Supramol. Chem. 6 (1995) 49.
[10] C.T. Dalton, K.M. Ryan, V.M. Wall, C. Bousquet, D.G. Gilheany, Top. Catal. 5 (1998) 75.
[11] W. Adam, K.J. Roschmann, C.R. Saha-Möler, D. Seebach, J. Am. Chem. Soc. 124 (2002) 5068.
[12] E.N. Jacobsen, M.H. Wu, in: A. Pfaltz, E.N. Jacobsen, H. Yamamoto (Eds.), Comprehensive Asymmetric Catalysis, vol. 2, Springer-Verlag, Berlin, 1999, p. 649.
[13] J.M. Fraile, J.I. García, J. Massam, J.A. Mayoral, J. Mol. Catal. A: Chem. 136 (1998) 47.
[14] L. Frunza, H. Kosslick, H. Landmesser, E. Hoft, R. Fricke, J. Mol. Catal. A: Chem. 123 (1997) 179.
[15] P.P. Knops-Gerrits, D.E. de Vos, P.A. Jacobs, J. Mol. Catal. A: Chem. 117 (1997) 57.
[16] A.R. Silva, M.M. Freitas, C. Freire, B. de Castro, J.L. Figueiredo, Microporous Mesoporous Mater. 46 (2001) 211.
[17] A.R. Silva, M. Martins, A. Valente, C. Freire, B. de Castro, J.L. Figueiredo, Microporous Mesoporous Mater. 55 (2002) 275.
[18] A.R. Silva, C. Freire, B. de Castro, J.L. Figueiredo, Langmuir 18 (2002) 8017.
[19] A.P. Carvalho, C. Castanheira, B. Cardoso, J. Pires, A.R. Silva, C. Freire, B. De Castro, M.B. de Carvalho, J. Mater. Chem. 14 (2004) 374.
[20] I. Neves, C. Freire, A.N. Zakhárov, B. de Castro, J.L. Figueiredo, Colloids Surf. A: Phys. Eng. Aspects 115 (1996) 249.
[21] R. Ferreira, M. Silva, C. Freire, B. de Castro, J.L. Figueiredo, Microporous Mesoporous Mater. 38 (2000) 391.
[22] S.P. Varkey, C. Ratnasamy, P. Ratnasamy, J. Mol. Catal. A: Chem. 135 (1998) 295.
[23] L.J. Boucher, J. Inorg. Nucl. Chem. 36 (1974) 531.
[24] L. Deng, E.N. Jacobsen, J. Org. Chem. 57 (1992) 4322.
[25] K.J. Balkus Jr., A.G. Gabrielov, J. Inclus. Phenom. Mol. Recogn. Chem. 21 (1995) 159, and references therein.
[26] M.M.J. Treacy, J.B. Higgins, Collection of Simulated XRD Powder Patters for Zeolites, 4th ed., Elsevier, Amsterdam, 2001.
[27] M. Silva, R. Ferreira, C. Freire, B. de Castro, J.L. Figueiredo, in: R. Aiello, G. Giordano, F. Testa (Eds.), Elsevier, Stud. Surf. Sci. Catal. 142A (2002) 879.
[28] A. Linares-Solano, in: J.L. Figueiredo, J.A. Moulijn (Eds.), Textural Characterization of Porous Carbons by Physical Adsorption of Gases, Carbon and Coal Gasification, Martinus Nijhoff Publishers, Dordrecht, 1986, p. 137.
[29] E. Paéz-Mozo, N. Gabriunas, F. Lucaccioni, et al., J. Phys. Chem. 97 (1993) 12819.
[30] T. Joseph, S.B. Halligudi, C. Satyanarayan, et al., J. Mol. Catal. A: Chem. 168 (2001) 87.
[31] V. Indira, S.B. Halligudi, S. Gopinathan, C. Gopinathan, React. Kinet. Catal. Lett. 73 (1) (2001) 99.
[32] A. Zsigmond, A. Horváth, F. Notheisz, J. Mol. Catal. A: Chem. 171 (2001) 95.
[33] A.N. de Sousa, M.E.M. Dai de Carvalho, Y.M. Idemori, J. Mol. Catal. A: Chem. 169 (2001) 1.
[34] K. Srinivasan, S. Perrier, J.K. Kochi, J. Mol. Catal. 36 (1986) 297.
[35] S.B. Halligudi, N.K. Kala Raj, S.S. Deshpande, S. Gopinathan, J. Mol. Catal. A: Chem. 157 (2000) 9.