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ChemPubSoc Europe



DOI:10.1002/ejic.201201517

# Electrochemical and Catalytic Studies of a Manganese(III) Complex with a Tetradentate Schiff-Base Ligand Encapsulated in NaY Zeolite

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Keywords: Electrochemistry / Heterogeneous catalysis / Oxidation / Zeolites / Manganese / Alkenes

The manganese(III) complex with a Schiff-base salen-type ligand  $(1,5-bis{[(1E)-(2-hydroxyphenyl)methylene]amino}-1H-imidazole-4-carbonitrile) has been encapsulated in the nanopores of a Y zeolite by using two different methodologies, the flexible ligand and in situ complex preparation methods. Cyclic voltammetry studies revealed that the neat complex undergoes reversible oxidation in dmf, which has been attributed to the Mn<sup>II/III</sup> redox couple, whereas the two heterogeneous catalysts show different electrochemical behaviour in aqueous medium. The encapsulated and non-$ 

# Introduction

Alkenyl and allylic oxidation reactions are of fundamental importance in synthetic organic chemistry, and a variety of reagents have been used for these transformations. The selectivity of the process depends on the oxygen source and solvent, however, the chemical properties of the ligand as well as the support also play a significant role. Selectivity in the allylic oxidation reaction in the presence of *tert*-butyl hydroperoxide (*t*BuOOH) is due to the ability of the *tert*butylperoxy radical to remove a hydrogen atom from the activated site with the lowest C–H bond dissociation energy.<sup>[1]</sup> Manganese–salen complexes are known to effectively catalyse the oxidation of olefins.

For practical use, the catalyst requires good stability against self-oxidation, which would lead to the formation of  $\mu$ -oxo dimers and peroxo-bridged compounds. Indeed, when molecular oxygen is used as the oxygen atom donor in homogeneous catalysis,  $\mu$ -oxo dimers are systematically formed in the medium causing a weakening of the oxidation

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encapsulated homogeneous Mn<sup>III</sup>salen complexes were screened as catalysts for olefin oxidation by using *t*BuOOH as the oxygen source in different solvents. Under the optimized conditions, the catalysts exhibited moderate activity. Both heterogeneous catalysts catalysed the oxidation of cyclohexene with *t*BuOOH, primarily to give the allylic oxidation products. These catalysts were found to be reusable after the catalytic cycle, but with some loss of activity. A DFT study confirmed the distortion of the complex in the zeolite cage, the main difference being observed for the bonded chloride.

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reaction due to their inactive catalytic character.<sup>[2,3]</sup> To overcome these difficulties, heterogenization of the catalyst has received considerable attention with different immobilization methods having been developed, for example, 1) intercalation into clays,<sup>[4]</sup> 2) encapsulation into zeolites or mesoporous molecular sieves<sup>[5–8]</sup> and 3) electropolymerization or grafting onto polymer matrices<sup>[9,10]</sup> or silicates.<sup>[11]</sup> It was concluded that the formation of  $\mu$ -oxo dimers is limited by immobilization, which consequently increases the turnover frequencies of the catalytic reaction.<sup>[12]</sup>

The use of zeolites for heterogenization has attracted considerable interest due to the size of the window pore, the accessibility of the void space, the dimensionality of the channel system and the number of sites and types of extra framework cations.<sup>[13]</sup> Faujasite zeolite, including zeolite X and Y, is frequently chosen as a support to encapsulate metal complexes because it presents large cavities or supercages (11.8 Å) with smaller pore openings (7.4 Å) that are suitable for accommodating metal complexes and a three-dimensional pore system desirable for easy reactant accessibility and product diffusion.<sup>[14,15]</sup> Metal complexes encapsulated into Y zeolite are interesting for applications as biomimetic heterogeneous catalysts for the oxidation of alkanes, alkenes and alcohols.<sup>[6,13–16]</sup>

Previously we have reported the redox proprieties of different metal complexes encapsulated in Y zeolite and showed that the electroactivity of zeolite-encapsulated



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of Inorganic Chemistry

metal complexes is related to the sites at which the complexes are incorporated.<sup>[5,17]</sup> The electroactivity is very important for understanding the stability of these heterogeneous catalysts in oxidation reactions.<sup>[9,18,19]</sup> As a continuation of this research, we report herein the electrochemical and catalytic properties of the manganese(III) complex formed with the Schiff base-salen-type ligand 1,5-bis{[(1*E*)-(2-hydroxyphenyl)methylene]amino}-1H-imidazole-4-carbonitrile, denoted as *salen*, in both homogeneous and heterogeneous media. These catalysts were tested in the oxidation of cyclohexene in the liquid phase with tBuOOH as the oxygen source. The effect of solvent on this oxidation reaction is reported and the catalytic activity of the Mn<sup>III</sup>salen complex is compared with that in the oxidation of styrene.<sup>[20]</sup> DFT studies were performed to rationalize the different electrochemical and catalytic behaviour arising from the different coordination sphere of the metal complex encapsulated in the NaY zeolite.



Figure 1. Cyclic voltammograms of  $H_2(salen)$  (grey) and [Mn(*salen*)Cl] (black) in dmf containing 0.10 M [NBu<sub>4</sub>][BF<sub>4</sub>] at room temperature under Ar recorded at a scan rate of 0.10 V s<sup>-1</sup> and at different potentials.

Table 1. Electrochemical data for the  $H_2(salen)$  ligand and [Mn(salen)Cl] complex.<sup>[a]</sup>

L	, 1 I						
v [V s <sup>-1</sup> ]	H <sub>2</sub> (	salen)	[Mn(salen)Cl]				
	Oxidation	Reduction	Oxic	Reduction			
	$E_{\rm p}^{\rm a}$ [V]	$-E_{\rm p}^{\ \rm c}$ [V]	$E_{\rm p}^{\rm a}$ [V]	$\Delta E [\mathrm{mV}]$	$-E_{\rm p}^{\ \rm c}$ [V]		
0.02	0.77	1.47	0.53	65	1.30		
0.05	0.78	1.48	0.54	80	1.32		
0.10	0.80	1.50	0.56	95	1.33		
0.20	0.81	1.51	0.59	100	1.34		
0.50	0.82	1.52	0.60	120	1.35		

[a] All measurements were taken at room temperature in degassed dmf with  $0.10 \text{ m} [\text{NBu}_4][\text{BF}_4]$  as the supporting electrolyte at a carbon working electrode. Potentials were measured with respect to ferrocenium/ferrocene as the internal standard. Finally, the potentials were converted and are reported relative to the SCE [*E*(fc<sup>+</sup>/fc) = 0.48 V vs. SCE].

# **Results and Discussion**

# Electrochemical Properties of the Neat and Encapsulated Mn<sup>III</sup>salen Complex

To gain some insights into the electron-richness of the complex studied, the electrochemical behaviour of the 1,5-bis{[(1E)-(2-hydroxyphenyl)methylene]amino}-1*H*-imid-azole-4-carbonitrile ligand, H<sub>2</sub>(*salen*), and its manganese complex, [Mn(*salen*)CI], were studied by cyclic voltammetry at different scan rates in dmf solutions containing 0.10 M [NBu<sub>4</sub>][BF<sub>4</sub>] as the supporting electrolyte. The electrochemical responses for the ligand and complex between the limits imposed by the solvent used are shown in Figure 1, and the most relevant data for the redox processes are summarized in Table 1.

The ligand shows one irreversible oxidation at 0.80 V versus SCE  $(E_p^a)$ , which can be attributed to the formation of the radical cation of the heterocyclic moiety, without any cathodic counterpart. At low potential, -1.50 V versus SCE  $(E_p^c)$ , this compound exhibits one irreversible electron process that generates a radical anion; the electron enters the  $\pi^*$  anti-bonding orbital of the heterocyclic ring.<sup>[21]</sup>

Cyclic voltammetry revealed that the manganese complex undergoes reversible oxidation in dmf solution (Figure 1, process IIa), which has been assigned to the Mn<sup>II/III</sup> redox couple  $[I_p^c/I_p^a \approx 1, \Delta E_p \approx (\text{ferrocenium/ferrocene})]$ . Comparison of the cyclic voltammograms obtained for the complex and the ligand in the positive potential range shows that after coordination it is not subject to the anodic process experienced by the ligand on oxidation. This can be explained by metal-to-heterocycle  $\pi^*$  orbital back-donation nitrogen atoms. Reduction of the complex occurs by an irreversible process (Figure 1, process Ic) and the reduction potential is shifted to a less cathodic value compared with the ligand.

The zeolite-encapsulated Mn<sup>III</sup>salen complex was deposited on Carbon Toray (CT) to determine the electroactivity and stability of the complex by cyclic voltammetry.<sup>[5,17]</sup> The voltammetric study was carried out in 0.10 M aqueous NaCl at room temperature. Under these conditions, the modified electrodes were mechanically and chemically stable. When the modified electrode was placed in the electrolytic solution and washed, no change in the colour of the solution was observed. The cyclic voltammograms of NaY-CT and Mnsalen@YA/B-CT in the positive potential range are presented in Figure 2. The cyclic voltammogram of NaY-CT did not exhibit any redox processes in the scan range of 0.50-1.40 V versus SCE. The cyclic voltammograms obtained for the modified electrodes Mnsalen@YA-CT and Mnsalen@YB-CT in this potential range did exhibit redox processes. The voltammogram obtained with the Mnsalen@YA-CT-modified electrode shows an anodic process at 0.98 V versus SCE with a cathodic counterpart at 0.63 V versus SCE. The Mnsalen@Y<sub>B</sub>-CT-modified electrode (Figure 2) shows an irreversible anodic process at 1.10 V versus SCE. The results of the electrochemical studies of the Mnsalen@YA-CT- and Mnsalen@YB-CT-modi-



fied electrodes show that their electrochemical behaviour is different, which is due to differences in the coordination sphere around the metal arising from the different encapsulation method used.



Figure 2. Cyclic voltammograms of NaY-CT (1), Mnsalen@Y<sub>A</sub>-CT (2) and Mnsalen@Y<sub>B</sub>-CT (3) at a scan rate of  $0.10 \text{ V s}^{-1}$ .

# Study of the Catalytic Properties of the Neat and Encapsulated Mn<sup>III</sup>salen Complex

The three catalysts were screened for the oxidation of olefins performed under aerobic conditions at room temperature. The results of the experiments performed with the new heterogeneous catalysts ( $Mnsalen@Y_A$  and  $Mnsalen@Y_B$ ) and its homogeneous counterpart ([Mn(salen)Cl]) in the oxidation of cyclohexene and styrene in different solvents are shown in Tables 2 and 3, respectively.

#### **Oxidation of Cyclohexene**

The Mn<sup>III</sup>salen heterogeneous catalysts were tested in the oxidation of cyclohexene in solvents of different polarity

[acetonitrile (acn) and decane] with tBuOOH as the oxygen source. The results obtained are summarized in Table 2 along with the data obtained with the homogeneous phase and the blank experiments under comparable conditions. The following reaction products were identified: cyclohexene oxide (CyO) as the alkenyl oxidation product and 2cyclohexen-1-ol (CyOl) and 2-cyclohexen-1-one (CyOne) as the allylic oxidation products. These products were also formed in the presence of a copper(II)-purine complex encapsulated in NaY zeolite<sup>[22]</sup> and electron-deficient manganese(III)-corrole<sup>[23]</sup> when tBuOOH was used as the oxygen source. Another significant product formed in this reaction was 1-tert-butylperoxy-2-cyclohexene (CyOx).[15] The formation of the allylic oxidation products (i.e., CyOne and CyOl) shows preferential attack of the activated C-H bond over the C=C bond. The selectivity for allylic oxidation by *t*BuOOH is due to the ability of the *tert*-butylperoxy radical to remove a hydrogen atom from the activated site having the lowest C–H bond dissociation energy.<sup>[1]</sup>

NaY and the blank experiments were performed, and the same cyclohexene conversion was observed (14%). In both cases only CyOx was detected. We have characterized this product previously<sup>[6]</sup> and it provides rather strong evidence for the involvement of the *t*BuOO<sup>•</sup> radical as the reactive intermediate. Marked improvement in substrate conversion, when compared with encapsulated complexes, resulted from the presence of the Mn<sup>III</sup>salen complex. Both heterogeneous catalysts show similar substrate conversions in decane compared with [Mn(*salen*)Cl] and higher conversions in acn.

Figure 3 shows representative examples of the results of the oxidation of cyclohexene in the homogeneous phase. It can be observed that the product distribution changed with time. A progressive reduction in CyOl and CyOne selectivity was observed under homogeneous conditions in the apolar solvent decane, whereas a different result was obtained in the aprotic polar medium acetonitrile, especially for CyOne.

Table 2. Oxidation of cyclohexene catalysed by the Mn<sup>III</sup>salen complex in homogeneous and heterogeneous phases.

Catalyst	Run	$T [h]^{[a]}$	C [%] <sup>[b,c]</sup>	Products							
2				CyO <sup>[d]</sup>		CyOl <sup>[e]</sup>		CyOne <sup>[f]</sup>		CyOx <sup>[g]</sup>	
				η [%] <sup>[h]</sup>	S [%] <sup>[i]</sup>	η [%]	S [%]	η [%]	S [%]	η [%]	S [%]
NaY	1	24	14 <sup>[j]</sup>	0	0	0	0	0	0	14	100
[Mn(salen)Cl]	1	5	48 <sup>[j]</sup>	2	5	2	5	9	10	34	71
Mnsalen@YA	1	48	45 <sup>[j]</sup>	5	11	3	8	14	31	23	50
0.11	2	48	24 <sup>[j]</sup>	2	9	1	6	3	12	18	73
Mnsalen@Y <sub>B</sub>	1	48	43 <sup>[j]</sup>	3	6	3	6	10	24	27	64
0 -	2	48	19 <sup>[j]</sup>	2	10	6	35	3	17	8	38
NaY	1	48	$< 1^{[1]}$	0	0	0	0	0	0	0	0
[Mn(salen)Cl]	1	5	42[1]	7	15	7	17	17	41	11	27
Mnsalen@YA	1	6	71 <sup>[1]</sup>	8	11	12	17	21	29	30	43
0	2	48	69[1]	26	38	4	6	24	34	15	22
Mnsalen@Y <sub>B</sub>	1	48	77[1]	18	24	15	20	23	29	21	27
0 5	2	48	36[1]	19	52	10	26	3	10	4	12

[a] Reaction time at which the substrate conversion becomes constant. [b] Determined by GC against an internal standard. [c] Cyclohexene conversion (*C*) was calculated as  $C = \{[A_{(cyclohexene)}/A_{(chlorobenzene)}]_{i=0h} - [A_{(cyclohexene)}/A_{(chlorobenzene)}]_{i=xh}\} \times 100/[A_{(cyclohexene)}/A_{(chlorobenzene)}]_{i=xh}\} \times 100/[A_{(cyclohexene)}/A_{(chlorobenzene)}]_{i=xh}$ 



Figure 3. Conversion/selectivity observed for the oxidation of cyclohexene in the presence of [Mn(salen)Cl] in (A) decane and (B) acn.

All the catalysts showed considerable selectivity towards CyO in acn. A small increase in the selectivity for CyO was observed in the presence of decane when the reaction was performed in the heterogeneous phase, nevertheless CyOne and CyOx were the main products. It seems that the zeolite not only protects the complex but also leads to an increase in the epoxide yield, as has been reported for other transition-metal complexes encapsulated in the zeolite Y.<sup>[24]</sup>

The effect of the solvent on the efficiency of manganesebased heterogeneous catalysts in the oxidation of cyclohexene has been widely studied recently.<sup>[25]</sup> These studies showed that the formation of CyOl increases with solvent polarity. This effect was also observed in our study in the first run, with the selectivity for CyOl being higher in acn than in decane. However, when Mnsalen@YA was used as the catatlyst and in the first cycle of Mnsalen@YB, the selectivity for CyOne was higher than CyOl independent of the solvent and in agreement with literature data.<sup>[25,26]</sup> The substrate conversion strongly depends on the properties of the complex as well as on the support materials, but less on the solvent as there is no wide-ranging relationship between these factors. Comparison of the conversions obtained with the two heterogeneous catalysts in apolar and polar solvents shows that both catalysts exhibit significantly higher activity in polar medium. This contrasts with the results of the reaction performed in the homogeneous phase. The difference might arise from different structures of the complex

(active site accessibility) under homogeneous and heterogeneous conditions.

Low catalytic activity ( $C_{\text{cvclohexene}} < 5\%$ ) was observed in the filtrate after removal of the catalyst, which indicates that the reaction was not fully catalysed heterogeneously and that a small amount of the active phase is leached into solution; this effect is less perceptible for Mnsalen@YA in acn. The FTIR spectra of the Mnsalen@Y<sub>A</sub> heterogeneous catalyst, as a representative example, measured before the catalytic reaction and after the second cycle show a decrease in band intensity in the region 1620–1100 cm<sup>-1</sup>. This corresponds to the frequency range in which vibration bands for the complex occur. Conversely, the bands typical of the zeolite matrix do not show significant changes after the catalytic reaction. These observations suggest that no structural changes of the zeolite matrix take place during consecutive catalytic cycles, but that some metal complex leaching must occur under the catalytic experimental conditions. Thus, the decrease in substrate conversion with reuse of the heterogeneous catalysts might be correlated with some leaching of the active phase.

In a previous study<sup>[15]</sup> we encapsulated other transitionmetal complexes within the NaY zeolite by using the flexible ligand method. These catalysts led to lower cyclohexene conversions and the selectivity for CyOne was always higher than the selectivity for CyOl, as was observed for the catalysts described in this report under the same experimental conditions. The different behaviour exhibited by the materials based on transition-metal complexes with PAN<sup>[15]</sup> and those presented in this work can be explained by considering the metal and its donor atoms. As was reported by Salavati-Niasari and co-workers,<sup>[26-28]</sup> the dgree of conversion of cyclohexene decreased in the following order: Mn > Co > Cu > Ni. The results obtained with the [Mn(salen)Cl]-based catalysts fits well in this series, and the substrate conversion decreases in the order Mn > Zn > Co > Cu when complexes have the same coordination mode, namely N2O2. However, the copper(II)-purine complex (N<sub>4</sub> coordination mode) encapsulated by the same method<sup>[22]</sup> shows higher cyclohexene conversion than the heterogeneous Mn<sup>III</sup>salen complex presented in this work under the same experimental conditions.

#### **Oxidation** of Styrene

It has been reported<sup>[29]</sup> that for neutral complexes such as [Mn(salen)]@NaY, leaching of the complexes into solution may occur, especially if the catalytic reaction is performed in a highly polar solvent. To overcome this problem, before the catalytic tests, the heterogeneous catalysts were subjected to Soxhlet extraction with a rather polar solvent, namely ethanol. To prove the Soxhlet efficiency and effect of solvent on the distribution of products, the reaction was screened in the polar solvents acn<sup>[20]</sup> and dichloromethane (dcm). Metal complexes encapsulated in the zeolite Y, including Mn<sup>III</sup>salens, can promote the formation of other products by the ring opening of phenyloxirane.<sup>[30–33]</sup> Under the experimental conditions used, the product distribution was the same as in the homogeneous oxidation of styrene

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with benzaldehyde as the major oxidation product followed by styrene epoxide. No other products were detected. The oxidation of styrene was negligible in the absence of heterogeneous transition-metal catalysts, which confirms that the oxidation is indeed catalytic in nature under these experimental conditions. The NaY zeolite without encapsulated metal complexes is also catalytically inactive. Therefore the Mn<sup>III</sup>salen</sup> complex encapsulated in the zeolite plays a determining role.

The experimental results obtained under homogeneous conditions confirmed that the [Mn(*salen*)Cl] complex shows excellent selectivity towards benzaldehyde (Bz) over the reaction period (Figure 4 and Table 3). This is in accordance with previous publications<sup>[32]</sup> in which only traces of phenylacetaldehyde were reported when the reaction was carried out in an homogeneous medium. Under these experimental conditions neither polymer nor benzoic acid formation was observed.<sup>[33]</sup> After the first 2 h of reaction, benzaldehyde was the major product with 95 and 100% selectivity in acn and dcm, respectively. After 5 h (acn) and 4 h (dcm), the selectivity towards styrene oxide (SO) increased to 30 and 20% in acn and dcm, respectively. No significant change in activity and product selectivity was observed after acquiring a steady state at around 6 h.

Compared with its homogeneous counterpart, the heterogeneous catalysts showed similar styrene conversion in the first reaction cycle. Both heterogeneous catalysts showed similar styrene epoxide selectivity in acn, although less than that observed for the homogeneous reaction. The NaY-supported catalysts after two cycles gave reduced styrene conversion for all catalyst systems, except  $Mnsalen@Y_B$  in acn. This has been observed with similar supported catalysts.<sup>[34]</sup>

To determine the cause of the decrease in styrene conversion upon catalyst reuse, the leaching test was carried out and the structural integrity of the catalysts was analysed by FTIR spectroscopy. Low catalytic activity was observed for the epoxidation of styrene in the filtrate after removal of



Figure 4. Conversion/selectivity for the oxidation of styrene in the presence of [Mn(*salen*)Cl] in (A) acn and (B) dcm.

the catalyst, which indicates that the reaction was not fully catalysed heterogeneously and that a small amount of leaching (the highest substrate conversion after catalyst removal was less than 10%) of the active phase into solution occurs. This effect was more perceptible when the reaction occurred in dcm. Although complex leaching was observed for all the catalysts, there is no direct correlation between the decrease in styrene conversion upon reuse and the Mn content after catalysis. This suggests that the decrease in

Catalyst	Run	T [h] <sup>[a]</sup>	$C [\%]^{[b,c]}$	Products				
•				S	0	Bz		
				$\eta \ [\%]^{[d]}$	S [%] <sup>[e]</sup>	$\eta ~[\%]^{[d]}$	S [%] <sup>[e]</sup>	
NaY	1	48	4 <sup>[f]</sup>	0	0	4	100	
[Mn(salen)Cl]	1	5	45 <sup>[f])</sup>	13	30	70	32	
Mnsalen@YA	1	<48	39 <sup>[f]</sup>	10	26	29	74	
0	2	4	12 <sup>[f]</sup>	<1	<1	11	99	
Mnsalen@Y <sub>B</sub>	1	5	40 <sup>[f]</sup>	10	26	30	74	
	2	24	54 <sup>[f]</sup>	12	23	42	77	
NaY	1	48	5 <sup>[g]</sup>	0	0	5	100	
[Mn(salen)Cl]	1	6	35 <sup>[g]</sup>	10	29	25	31	
Mnsalen@YA	1	48	37 <sup>[g]</sup>	5	14	32	86	
	2	48	14 <sup>[g]</sup>	1	9	13	91	
Mnsalen@Y <sub>B</sub>	1	48	48 <sup>[g]</sup>	13	27	35	73	
0 -	2	48	8 <sup>[g]</sup>	5	62	3	38	

Table 3. Oxidation of styrene catalysed by the [Mn(salen)Cl] complex in the homogeneous and heterogeneous phases.

[a] Reaction time at which the substrate conversion becomes constant. [b] Determined by GC against an internal standard. [c] Styrene conversion (C) calculated as  $C = \{[A_{(styrene)}/A_{(chlorobenzene)}]_{t=0h} - [A_{(styrene)}/A_{(chlorobenzene)}]_{t=0h} \times 100/[A_{(styrene)}/A_{(chlorobenzene)}]_{t=0h}; A = chromatographic peak area. [d] Product yield (\eta) calculated as <math>\eta = CS/100$ . [e] Product selectivity (S) calculated as  $S = A_{(product)} \times 100/[A_{(product)} + \Sigma A_{(other reaction products)}]; A = chromatographic peak area. [f] In acn.<sup>[20]</sup> [g] In dcm (this work).$ 

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styrene conversion is determined not only by complex leaching, but also by some metal complex deactivation during the catalytic cycles. The catalytic centres can be deactivated by decomposition of the complex inside the matrix by the oxidant<sup>[35]</sup> or by parallel reactions that involve the formation of dimeric  $\mu\text{-}oxo\text{-}Mn^{IV}$  species, which are inactive towards styrene epoxidation, as observed in homogeneous solution.<sup>[2]</sup> The occurrence of the latter reaction is less probable especially because of the dimensions of these molecules as well as the difficulties in complex diffusion from the zeolite cage. The FTIR spectra for both heterogeneous catalysts recorded after the second reuse show band broadening in the  $1620-1200 \text{ cm}^{-1}$  region, which corresponds to the frequency range in which bands due to the complex occur. During the catalytic cycles, no structural changes in the zeolite matrix took place, but some metal complex leaching and/or decomposition must occur under the catalytic experimental conditions, which supports the results obtained upon reuse of the catalyst. It can be concluded that the catalytic oxidation ability of the catalysts presented in this work depends on the structure of the complex and the polarity of the reaction medium.

## DFT Studies of the Neat and Encapsulated Mn<sup>III</sup>salen Complex

DFT studies were performed to verify the structures of the Mn<sup>III</sup>salen complex encapsulated in NaY obtained by different methods. It is well known that Schiff-base salentype ligands react with different metal ions to give intensely coloured chelate complexes. They act as tetradentate ligands coordinating the metal through the hydroxy oxygen atoms and the azomethine nitrogen atoms. The complex [Mn(salen)Cl] shows a slightly distorted square-pyramidal geometry. The molecular structure of the neat Mn(III)salen complex was optimized in the gas phase at the B3LYP/6-31G(d,p) level of theory without any symmetry constraints and the final geometry is depicted in Figure 5a. The optimized structure shows a square-pyramidal configuration of the chromophore with coordination through the two oxygen and two nitrogen atoms in the Schiff-base ligand and the chloride ion (Figure 5a).

The geometry of the Mn<sup>III</sup>salen complex in the cage of the NaY zeolite (see Figure 5b) reveals some distortion of the square-pyramidal geometry found in the gas phase. The most relevant geometrical parameters are collected in Table 4. The distances between the metal ion and the nearest atoms are practically the same for the complex in the gas phase and inside the zeolite cage. However, a noticeable perturbation is observed in the Mn–Cl distance, which is significantly shortened (more than 0.1 Å) when the complex is encapsulated in the zeolite cage. The most notable differences are observed in the values of the bond and dihedral angles around the metal ion. These results show that the chlorine atom is closer to nitrogen N1 inside the zeolite than in the neat complex, which has a more regular geometry. These distortions in the structure of the complex upon



Figure 5. Optimized structures: (a) top and side views of the neat complex in gas phase and (b) Mn(III)*salen* complex encapsulated into the NaY zeolite.

encapsulation might have some influence on the FTIR spectra of the zeolite-based materials.

Table 4. Optimized values of the most relevant geometrical parameters of neat  $[Mn(salen)Cl]^{[a]}$  and inside the zeolite.<sup>[b]</sup>

Distance [Å]	[Mn(salen)Cl]	Mnsalen@Y
MnCl	2.327	2.206
Mn-N1	2.034	2.069
Mn–N2	2.027	1.977
Mn-O1	1.873	1.820
Mn–O2	1.863	1.845
Angle [°]		
N1–Mn–N2	87.02	79.60
O1–Mn–O2	92.57	90.79
N1-Mn-O1	87.98	85.62
N2-Mn-O2	89.95	93.23
N1-Mn-O2	157.06	163.66
N2-Mn-O1	156.21	140.09
N1-Mn-Cl	95.22	88.80
N2-Mn-Cl	96.67	104.07
O1-Mn-Cl	105.21	112.51
O2-Mn-Cl	106.71	107.26
Dihedral angle [°]		
N1-01-02-N2	-22.00	-14.81

[a] Determined at the B3LYP/6-31G(d,p) of theory. [b] Determined at the ONIOM [B3LYP/6-31G(d,p):PM6] level of theory.

The most representative IR frequencies of the optimized complex are presented in Table 5. The theoretical predictions of the vibrational frequencies for the neat and encap-

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sulated complex show the same shifts as observed in the experimental FTIR spectra.<sup>[20]</sup> Moreover, the band positions are in good agreement for neat and encapsulated complexes.

Table 5. Representative experimental and theoretical IR frequencies for neat  $[Mn(salen)Cl]^{[a]}$  and inside of the zeolite.<sup>[b]</sup>

			v [cm <sup>-1</sup> ]					
		$C \equiv N$	C=N	Arom.	C=N <sup>[c]</sup>	С–О	$C - H^{[d]}$	
[Mn(salen)Cl]	Exp.[e]	2222	1602	1566	1485	1384	1282	
	Theor.	2342	1633	1577	1484	1345	1279	
Mn(salen)@Y	Exp. <sup>[e]</sup>	2219	1585	1541	1475	1396	1300	
	Theor.	2341	1620	1570	1457	1357	1274	

[a] Determined at the B3LYP/6-31G(d,p) of theory. [b] Determined at the ONIOM [B3LYP/6-31G(d,p):PM6] of theory. [c] In the imidazole ring. [d] In-plane deformation. [e] From  $ref.^{[20]}$ 

The DFT studies show that the molecular structure of the Mn<sup>III</sup>salen complex encapsulated in NaY corresponds to the catalyst obtained by in situ method (A) in which the counter ion is chloride. However, for the catalyst obtained by the flexible ligand method (B), the counter ion is the oxygen from the zeolite framework. This means that chloride and oxygen complete the square-pyramidal coordination of Mn<sup>III</sup> when methods A and B, respectively, are used.

#### Conclusions

The manganese(III) complex with the tetradentate Schiff base derived from 1,5-bis{[(1*E*)-(2-hydroxyphenyl)methylenelamino}-1H-imidazole-4-carbonitrile was encapsulated in the Y zeolite by using two different methodologies: in situ complex preparation (A) and the flexible ligand method (B). The two methodologies lead to a different coordination sphere around the manganese. Cyclic voltammetry studies of the neat complex in dmf and the heterogeneous catalysts in aqueous medium showed different electrochemical behaviour. The neat complex [Mn(salen)Cl] shows a reversible oxidation process, which has been assigned to the Mn<sup>II/III</sup> redox couple. The modified electrode of the heterogeneous catalyst obtained by method A shows a quasi-reversible process, whereas the modified electrode of Mnsalen@YB-CT shows an irreversible anodic process. In the catalytic studies, the heterogeneous catalysts led to similar or higher substrate conversions than the homogeneous catalyst. When acn was used as solvent, both heterogeneous catalysts led to a higher conversion of cyclohexene compared with styrene under the same conditions. The substrate conversion depends of the encapsulation method used and the supporting material. DFT studies confirmed some distortion of the complex geometry during the encapsulation.

## **Experimental Section**

**Materials and Reagents:** NaY zeolite (CBV100, Si/Al ratio = 2.83) in powder form was obtained from Zeolyst International. NaY powder was calcined at 500 °C for 8 h under a dry stream of air prior to use. All chemicals and solvents were reagent-grade and

purchased from Aldrich: 2-hydroxybenzaldehyde, manganese(II) chloride tetrahydrate (MnCl<sub>2</sub>·4H<sub>2</sub>O), triethylamine, acetonitrile (acn), dichloromethane (dcm), decane, ethanol, *tert*-butyl hydroperoxide solution, 5.0–6.0 M in decane (*t*BuOOH), chlorobenzene (PhCl), cyclohexene and styrene. Nafion solution (Nafion<sup>®</sup> 117 solution) was purchased from Aldrich and Carbon Toray from Quintech. Spectroscopic-grade potassium bromide used for the preparation of FTIR pellets was purchased from Merck.

Encapsulation of the Mn<sup>III</sup>salen Complex in NaY: The synthesis and characterization of the Schiff-base ligand 1,5-bis{[(1E)-(2-hydroxyphenyl)methylene]amino}-1*H*-imidazole-4-carbonitrile, denoted as H<sub>2</sub>(salen), and the corresponding manganese(III) complex, denoted as [Mn(salen)Cl] has been reported by us elsewhere,<sup>[20]</sup> as well as the encapsulation of the Mn<sup>III</sup>salen complex guest by two different methodologies.<sup>[20]</sup> The catalyst prepared by in situ complex formation was obtained by using the general method.<sup>[20]</sup> Briefly, a solution of the H<sub>2</sub>(salen) ligand and hydrated Mn<sup>II</sup> chloride in ethanol was added to a suspension of NaY zeolite and then triethylamine was added. Uncomplexed ligand and the molecules of the complex adsorbed on the external surface were removed by Soxhlet extraction with ethanol. The extracted sample was further washed with deionized water to remove undesired metal ions. The new catalyst (Mnsalen@YA) was dried overnight under reduced pressure. The manganese content in Mnsalen@YA was 0.55%.

The flexible ligand immobilization method starts with cation exchange in the NaY zeolite by using an aqueous solution of hydrated  $Mn^{II}$  chloride. MnY solid was suspended in a solution of the H<sub>2</sub>(*salen*) ligand in ethanol and then triethylamine was added. The new material was Soxhlet extracted with ethanol and dcm to remove unreacted ligand. The new catalyst (Mnsalen@Y<sub>B</sub>) was dried overnight under reduced pressure. The manganese content in Mnsalen@Y<sub>B</sub> was 0.80%.

Methods of Characterization: The elements Si, Al, Na and Mn were quantitatively analysed by inductively coupled plasma atomic emission spectrometry (ICP-AES) using a Philips ICP PU 7000 spectrometer. FTIR spectra of solid samples were obtained with a Bomem MB104 spectrophotometer at room temperature from powdered samples mixed with KBr to form pellets for measurement. CV was performed by using a potentiostat/galvanostat (AUTOLAB/PSTAT 12) with the low-current module ECD from ECO-CHEMIE and the data analysis was processed by using the General Purpose Electrochemical System software package also from ECO-CHEMIE. Three electrode-two compartment cells equipped with vitreous carbon disc working electrodes, a platinum wire secondary electrode and a silver wire pseudo-reference electrode were employed for cyclic voltammetric measurements. The concentration of the free complex was 1.0 mM and 0.10 M [NBu<sub>4</sub>][BF<sub>4</sub>] was used as the supporting electrolyte in dry dmf. Cyclic voltammetry was usually conducted at 0.10 Vs<sup>-1</sup> or at different scan rates  $(0.02-0.50 \text{ V s}^{-1})$  to investigate the influence of the scan rate. Potentials were measured with respect to ferrocenium/ferrocene as an internal standard. Voltammetric measurements on zeolite-based materials were carried out with a computerized AMEL instrument General-purpose Potentiostat model 2051. The experiments were controlled with the home-made program LAB VIEW. All electrochemical studies were performed at room temperature with a three-electrode assembly including a 250 mL glass cell, a saturated calomel electrode as reference electrode, a 90% platinum and 10% iridium counter electrode and the working electrode was Carbon Toray (CT) or CT modified by manganese salen complexes encapsulated in zeolite NaY. All potentials were measured and rewww.eurjic.org

ported versus the SCE reference electrode. The GC-FID chromatograms were obtained with a SRI 8610C chromatograph equipped with a CP-Sil 8CB capillary column. Nitrogen was used as the carrier gas. The identification of reaction products was confirmed by GC–MS (Varian 4000 Performance).

Computational Details: All the calculations were performed in the gas phase and the corresponding relative energies were calculated by the one-layer, single method, and two-layer, ONIOM method,<sup>[36]</sup> by using B3LYP<sup>[37]</sup> for the high-level calculations and PM6<sup>[38]</sup> for the low-level calculations. The geometry of the neat [Mn(salen)Cl] complex was characterized by a quantum mechanical method based on DFT. The B3LYP Becke's three-parameter exchange-correlation hybrid functional with non-local correlation corrections provided by Lee, Yang and Parr was used.<sup>[37]</sup> The double-zeta Pople basis set 6-31G(d,p) was employed, which ensures a superior electronic description by adding polarization functions of the p-, dand, especially, f-type for all the hydrogen atoms and non-hydrogen atoms and metal ions, respectively. When encapsulated in the NaY zeolite cage, the geometry of the [Mn(salen)Cl] complex was optimized by using the two-layer ONIOM [B3LYP/6-31G(d,p):PM6] method in which the B3LYP/6-31G(d,p) method was used for the high-level calculation for the [Mn(salen)Cl] complex and the semiempirical PM6 method was used for the low-level calculation for the zeolite framework. The geometry of the NaY zeolite, faujasitetype structure, was taken from the database of the Structure Commission of the International Zeolite Association (IZA).<sup>[39]</sup> The vibrational frequencies of these optimized structures were predicted by using the same basis set. No imaginary frequencies were obtained, which confirms that the molecular structures were optimized at stationary positions on the potential energy surface. Usually, the harmonic frequencies calculated at the B3LYP/6-31G(d,p) level have to be scaled,<sup>[40]</sup> however, the agreement between theoretical and experimental results was so satisfactory in this work that further scaling of the calculated frequencies seemed unnecessary. All geometry optimizations and energy and frequency calculations were performed by using the Gaussian 09 package of programs.<sup>[41]</sup> Graphical representations of the optimized structures and the molecular orbitals were produced with the MOLEKEL 4.3<sup>[42]</sup> and Gauss-View molecular visualization programs.<sup>[43]</sup>

**Preparation of Zeolite-Modified Electrodes:** The preparation of the zeolite-modified electrodes was based on a previous established procedure.<sup>[5]</sup> To prepare the zeolite-modified electrodes, 20 mg of the heterogeneous catalyst was suspended in a Nafion/water solution (120  $\mu$ L Nafion/120  $\mu$ L ultra-pure water). The resulting solutions were homogenized by using an ultrasound bath and deposited on Carbon Toray paper with an area of  $2 \times 2$  cm<sup>2</sup>. The carbon was used to increase the area of electrical conductor in direct contact with the zeolite. Finally, the Carbon Toray paper was glued to the platinum electrode by using conductive carbon cement (Quintech) and dried at room temperature for 24 h.

**Catalytic Oxidation Reactions:** The oxidation of cyclohexene and styrene was studied under argon with constant stirring at room temperature. The composition of the reaction medium was alkene (0.1 g, 1.0 mmol), internal standard (0.1 g, 1.0 mmol) and heterogeneous catalyst (0.10 g) in different solvents (5.0 mL), acn, dcm and decane. *t*BuOOH (0.3 mL, 1.65 mmol, 5.5 M in decane solution) was progressively added to the reaction medium at a rate of  $0.05 \text{ mLmin}^{-1}$ . The progress of the reaction was monitored as a function of time by withdrawing samples at fixed time intervals and analysing them by gas chromatography. The identities of the products were confirmed by comparison with authentic samples or by GC–MS. The products were quantitatively determined by the

internal standard method. After each reaction cycle, the catalysts were washed, dried and characterized. The catalytic activity of homogeneous [Mn(*salen*)Cl] was also tested; the amount of neat complex was equivalent 0.50% Mn relative to alkene.

### Acknowledgments

I. K.-B. thanks the Fundação do Ministério de Ciência e Tecnologia (FCT) for a contract under the program Ciência 2007. The authors thank the FCT and the Fundo Europeu de Desenvolvimento Regional (FEDER)) [COMPETE-QREN-EU, grant number PEst-C/QUI/UI0686/2011 (FCOMP-01-0124-FEDER-022716)] for financial support to the Research Centre at the Centro de Química, Universidade do Minho.

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Received: December 14, 2012

Pages: 10



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Electrochemical and Catalytic Studies of a Manganese(III)Complex with a Tetradentate Schiff-Base Ligand Encapsulated in NaY Zeolite

Keywords: Electrochemistry / Heterogeneous catalysis / Oxidation / Zeolites / Manganese / Alkenes



Two methods for the encapsulation of a Mn<sup>III</sup>salen complex in NaY zeolite lead to different modes of coordination at the metal. Cyclic voltammetry of the neat and heterogeneous complexes shows different electrochemical behaviour. The heterogeneous catalysts lead to similar or higher alkene conversion than the homogeneous catalyst. DFT confirmed distortion of the complex in a confined space.

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