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# Manganese complexes with triazenido ligands encapsulated in NaY zeolite as heterogeneous catalysts

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#### 1. Introduction

Selective catalytic oxidation of alcohols to carbonyls is one of the most important chemical transformations in industrial chemistry. Carbonyl compounds such as ketones and aldehydes are the precursors for many drugs, vitamins, and fragrances and they are also important intermediates for many complex syntheses [1,2]. The catalytic epoxidation of terminal and electron-deficient olefins also constitutes a challenging task in organic chemistry. Transition metal complexes are successfully used to catalyse these reactions in homogeneous reaction media. The separation and recycling of homogeneous catalysts is problematic, often making the entire catalytic process economically unviable for industrial processes. The heterogenization of homogeneous catalysts has therefore become an important strategy to obtain supported catalysts that retain the homogeneous catalytic sites with the advantages of easy separation and recycling [3]. As a consequence, zeolites have been preferred hosts for the encapsulation/immobilization of transition metal complexes [3,4].

Zeolites are hydrated aluminosilicate crystalline solids with very regular microporous structures in which active and chemically interesting compounds can be included. Apart from the space constraints imposed by the zeolite, their exchangeable properties due to the negative charge of the framework and the distribution of the positive charges of the cations can lead to specific interac-

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## ABSTRACT

Two different methods were described for the preparation of manganese complexes with triazenido derivative ligands encapsulated in NaY zeolite. The catalytic behaviour of the heterogeneous catalysts was evaluated for styrene and cyclohexanol oxidation reactions. Encapsulation was achieved by two methods: (i) ion-exchange from an ethanol solution containing both bis(*p*-tolyl)triazenido ligand and manganese ions, with the ligand: Mn 3:1 molar ratio (Method A) and (ii) the flexible ligand method (Method B). The heterogeneous catalysts were characterized by FTIR spectroscopy, X-ray photoelectron spectroscopy (XPS), powder X-ray diffraction (XRD) and chemical analyses. The results show that both preparation methods lead to effective encapsulation of the Mn{bis(*p*-tolyl)triazenido} (1:1) complex in the NaY zeolite framework. The heterogeneous catalysts show activity in oxidation of styrene and cyclohexanol with *tert*-butyl hydroperoxide (*t*BuOOH) as an oxygen source. The catalysts are chemo-selective in cyclohexanol oxidation, whereas in styrene oxidation reaction leads to styrene oxide and benzaldehyde.

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tions with the inserted chemical compounds [3–5]. Zeolite cages increase the protection of complex molecules from decomposition and irreversible dimerization by providing steric constraints around the molecule [5–7]. Y zeolite is frequently chosen as a host to encapsulate metal complexes because of its large supercages (11.8 Å) with smaller pore openings (7.4 Å) suitable for the accommodation of metal complexes and three-dimensional pore network desirable for easy reactant accessibility and product diffusion [3–7]. The host supplies additional stability of the incorporated metal complex, thereby extending the physical and chemical resistance of the catalyst [8].

The development of novel ligands capable of forming stable complexes that can be used as effective catalysts in organic synthesis is an important field in organometallic chemistry [9]. Nitrogen-donor ligands have received much attention, including the  $\beta$ -diketiminate and the amidinate ligand systems [10–12]. Minor attention has been given to triazenides ligands [13,14]. The triazenides are able to form strong metal–nitrogen bonds and successfully stabilise the complexes formed. These complexes were successfully synthesised [15–20]. However, few of them have been developed as homogeneous catalysts [21]. To the best of our knowledge, there are no studies with these complexes as heterogeneous catalysts in oxidation reactions.

The usual method for the introduction of metal complexes into the zeolite structure is the *flexible ligand* method. In this approach, the ligand is added to the metal ion exchanged in zeolite [22–29]. *In situ* complex preparation within the zeolite also has been used. In this method, the ligand and the metal ion are added simulta-





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neously to the liquid phase inside the zeolite with subsequent coordination [1,30–34]. It may be expected that different encapsulation methods would result in different catalytic properties of the resulting heterogeneous catalysts [30,35,36]. Initial studies used the *in situ* method and showed that the Y-encapsulated transition metal complexes presented a good catalytic activity in the oxidation of alcohols and alkenes [31–34]. In this research two different methods were used for *in situ* encapsulation of manganese complexes with the triazenido ligand in NaY zeolite framework. Catalytic studies were performed in the liquid phase for the oxidation of cyclohexanol and styrene, using *tert*-butyl hydroperoxide (*t*BuOOH) as an oxygen source.

#### 2. Experimental

#### 2.1. Materials and reagents

NaY zeolite (Si/Al = 2.83) in powdered form was obtained from Zeolyst International. The powder it was calcined at 500 °C for 8 h under a dry air stream prior to use. All chemicals and solvents used were reagent grade and purchased from Aldrich: manganese(II) chloride tetrahydrate (MnCl<sub>2</sub>·4H<sub>2</sub>O), manganese(II) sulfate monohydrate (MnSO<sub>4</sub>·H<sub>2</sub>O), triethylamine, acetonitrile, dichloromethane, ethanol, *tert*-butyl hydroperoxide solution – 5.0–6.0 M in decane (*t*BuOOH), chlorobenzene, cyclohexanol and styrene. Spectroscopic grade potassium bromide (KBr) used for the FTIR pellets preparation was supplied by Merck.

#### 2.2. Synthesis of 1,3-bis(tolyl)triazene and free complex

1,3-Bis(tolyl)triazene (dtta) was synthesized following the literature procedures [37]. Triazene was obtained by coupling of *p*-toluidine, in toluene using isoamyl nitrite and isolated by crystallization from ethyl acetate/hexane (4:1) at 0 °C with a yield of 78%. As yellow crystals; m.p. 162 °C. FTIR (KBr,  $\nu/\text{cm}^{-1}$ ): 1612 [ $\nu$ (N=N)]; 3198 [ $\nu$ (N-H)]. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.30 (s, 6H, 2CH<sub>3</sub>), 7.0 and 7.3 (AX pattern, 8H,  $J_{AX}$  = 9 Hz,  $C_6H_4$ CH<sub>3</sub>), 7.9 (s, 1H, NH). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  = 142.8 ( $C_{Ar}$ -N), 138.7 ( $C_{Ar}$ -H), 132.8 ( $C_{Ar}$ -H), 129.5 ( $C_{Ar}$ -H), 128.1 ( $C_{Ar}$ -CH<sub>3</sub>), 123.2 ( $C_{Ar}$ -H), 21.2 (Ar-CH<sub>3</sub>). Anal. Calc. for  $C_{14}H_{15}N_3$ : C, 74.64; H, 6.71; N, 18.65. Found: C, 74.51; H, 6.64; N, 18.81%.

Free complex was synthesized by addition of a solution of dtta (76 mg, 0.34 mmol) in 25 mL of ethanol to a solution of manganese(II) chloride tetrahydrate (20 mg, 0.10 mmol) in the same solvent. The reaction mixture was stirred and then triethylamine (0.5 mL, 3.5 mmol) was added. A 4 mL of hexane was added to the resulting brown solution and brown-green crystals started to precipitate after 10 h. The solid was filtered off, washed with diethyl ether and hexane, and then dried under vacuum to obtain a yield of 74% (0.04 g). *Anal.* Calc. for MnClC<sub>28</sub>H<sub>28</sub>N<sub>6</sub>: C, 62.40; H, 5.24; N, 15.59. Found: C, 62.27; H, 5.18; N, 16.02%. FTIR ( $\nu$ / cm<sup>-1</sup>): 1525 [ $\nu$ (N=N)]. UV/Vis ( $\lambda_{max}/nm$ ): 290 and 360. HRMS (NBA): m/z = 538.14228 [M]<sup>+</sup>; Calc. for MnClC<sub>28</sub>H<sub>28</sub>N<sub>6</sub> 538.14389.

#### 2.3. Methods for the preparation of the heterogeneous catalysts

#### 2.3.1. Method A

A solution of dtta ligand (77 mg, 0.34 mmol) and manganese(II) chloride tetrahydrate, (20 mg 0.10 mmol) in 25 mL of ethanol was added to NaY zeolite suspension (1.0 g in 25 mL of ethanol). A volume of 0.5 mL (3.58 mmol) triethylamine was added to the mixture with stirring for 12 h at room temperature. The solid fraction was filtered off. Uncomplexed ligand and the complex molecules adsorbed on the external surface were removed through Soxhlet extraction with ethanol until the eluate became colourless.

The extracted sample was further washed with a solution of NaCl in deionised water to ion-exchange undesired free metal ions. The resulting catalyst, designated as  $Mn(dtta)-Y_A$ , was dried in an oven at 60 °C overnight under reduced pressure.

#### 2.3.2. Method B

NaY Zeolite was first ion-exchanged with an aqueous solution of manganese(II) sulphate monohydrate (0.01 mol/L, liquid/solid = 130 mL/g) at pH 5.3 with stirring for 12 h at room temperature. The solid obtained was washed with deionised water and dried at 80 °C overnight under reduced pressure. Mn-Y solid (1.5 g) was suspended in a solution of 1.35 g (6 mmol) of ligand in 50 mL of ethanol and then six drops of triethylamine were added. The mixture was stirred for 24 h at room temperature. The resulting solid was filtered off and washed with deionised water and ethanol, then dried at 60 °C under reduced pressure overnight. The solid was Soxhlet extracted with ethanol and again with dichloromethane to remove the unreacted ligand, till the eluate became colourless. The extracted sample was further washed with a solution of NaCl in deionised water to ion-exchange undesired free metal ions. The catalyst, Mn(dtta)-Y<sub>B</sub>, was dried in an oven at 60 °C overnight under reduced pressure.

#### 2.4. Characterisation methods

NMR spectra were obtained with a Varian Unity Plus Spectrometer at an operating frequency of 300 MHz for <sup>1</sup>H NMR and 75.4 MHz for <sup>13</sup>C NMR or with a Bruker Avance III 400 at an operating frequency of 400 MHz for <sup>1</sup>H NMR and 100.6 MHz for <sup>13</sup>C NMR using the solvent peak as internal reference at 25 °C. X-ray photoelectron spectroscopy (XPS) was performed at the Centre for Scientific Support Technology and Research, University of Vigo, Spain, using a VG Scientific spectrometer ESCALAB 250 iXL with non-monochromatised Al K $\alpha$  radiation (1486.6 eV). Charge referencing was done by setting the lower binding energy C 1s photopeak at 285.0 eV. The atomic concentrations were determined from the XPS peak areas using the Shirley background subtraction technique and Scofield sensitivity factors. The XPS high-resolution spectra were fitted using a Gaussian-Lorentzian line shape, Shirley background [38] and damped non-linear least-squares procedure. The line-width of the Gaussian peak (full-width at half maximum, FWHM) was optimised for all components on each individual highresolution spectrum. Chemical analysis of C, H and N were carried out on a Leco CHNS-932 analyzer. High-resolution mass spectra (HRMS) were obtained with a GV AutoSpec spectrometer using an *m*-nitrobenzyl alcohol (NBA) matrix. Mn loading on zeolitic samples was evaluated according to the SMEWW 3120 method, using Inductive Coupled Plasma (ICP) performed in the Instituto Superior Técnico in Portugal. Powder X-ray diffraction patterns (XRD) were recorded using a Philips Analytical X-ray model PW1710 BASED diffractometer system. The solids samples were exposed to the Cu Ka radiation at room temperature in a  $2\theta$  range between 5° and 65°. Fourier Transform Infrared (FTIR) spectra of the materials were obtained as KBr pellets, mixed in 1:150 ratio (material:KBr), in the range of  $500-4000 \text{ cm}^{-1}$ , with a BOMEM MB 10 spectrophotometer. All spectra were collected at room temperature, with a resolution of 4 cm<sup>-1</sup> and 32 scans. The electronic UV-Vis absorption spectra of the free complex was collected in the range 600-200 nm in a Shimadzu UV/2501PC spectrophotometer using quartz cells at room temperature. The GC-FID chromatograms were obtained with a SRI 8610C chromatograph equipped with 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).

#### 2.5. Catalytic experiments

#### 2.5.1. Oxidation of styrene

Epoxidation of styrene was studied under an argon atmosphere with constant stirring at room temperature. Briefly, 0.10 g (0.1 mmol) of styrene, 0.10 g (0.1 mmol) of chlorobenzene (internal standard) and 0.10 g of heterogeneous catalyst were mixed in 5.0 mL of acetonitrile; tBuOOH (0.3 mL of 5.5 M in decane solution, oxygen source) was progressively added to the reaction at a rate of 0.05 mL min<sup>-1</sup>. During the experiments, 0.1 mL aliquots were taken from solution with a hypodermic syringe, filtered through 0.2 µm syringe filters and directly analysed by GC. After the reaction cycle, the catalysts were washed, dried and characterized.

#### 2.5.2. Oxidation of cyclohexanol

The reaction was carried out in 4.0 mL of acetonitrile at 40 °C ( $\pm$ 5 °C) under an argon atmosphere with constant stirring, and the composition of the reaction medium was cyclohexanol (0.6 mL, 5.8 mmol), chlorobenzene as internal standard (0.6 mL, 5.9 mmol) and 0.10 g of heterogeneous catalyst. The oxidant, *t*BuOOH (2.0 mL of 5.5 M in decane solution), was progressively added to the reaction medium at a rate of 0.1 mL min<sup>-1</sup> using a KD Scientific Syringe Pump: KDS 200P. The reaction products were analysed and identified as mentioned above.

At the end of each run, the heterogeneous catalysts were sequentially extracted/centrifuged three times with 10.0 mL of ethanol and two times with 10.0 mL of acetonitrile, and then dried in an oven at 100  $^{\circ}$ C overnight before a new catalytic cycle was initiated and characterized by FTIR.

#### 3. Results and discussion

#### 3.1. Synthesis and characterization

The free complex synthesized in this study by reaction of manganese chloride with bis(*p*-tolyl)triazene (dtta) in ethanol is described in Scheme 1.

Manganese chloride tetrahydrate reacts with 1,3-bis(*p*-tolyl)triazene in the presence of triethylamine, in refluxing ethanol, to obtain the brown air-stable complex [MnCl(1,3-bis(tolyl)triazenido)<sub>2</sub>], [MnCl(dtta)<sub>2</sub>]. The infrared spectrum shows the band of absorptions expected for coordinated triazenido ligand. In particular the v(N-H) vibration band of the free triazene at 3198 cm<sup>-1</sup> is absent in the complex spectrum and the vibration band attributed to v(N=N) is shifted from 1612 (free ligand) to 1525 cm<sup>-1</sup> (complex). This shift observed has been attributed to  $\pi$ -bonding between the d orbitals of the metal and  $\pi^*$  orbital of triazenido group, which leads to a variation in N=N bond order [39]. These observations show that the triazen-



**Scheme 1.** Synthesis of free complex [MnCl(1,3-bis(tolyl)triazenido)<sub>2</sub>].

CH

ĊH-

 $H_2$ 

ido ligand is coordinated in chelating form. Elemental analysis and spectroscopic results are in agreement with the assumed structure, where presented two chelates dtta ligands and one chloride atom.

NaY zeolite was used as a host in different encapsulation methods in order to obtain stable heterogeneous catalysts for oxidation reactions (Scheme 2).

In method A, the manganese ion and dtta ligand were added simultaneously to zeolite suspension in ethanolic medium. In method B, the *in situ* encapsulation was achieved by the ion exchange of the manganese ion in aqueous medium followed by the insertion of the dtta ligand in the framework of the zeolite upon its complexation.

The heterogeneous catalysts were characterized by infrared spectroscopy (FTIR), powder X-ray diffraction (XRD), chemical analyses and X-ray photoelectron spectroscopy (XPS).

The FTIR spectra obtained for NaY and the catalysts are illustrated in Fig. 1. The spectrum of NaY zeolite is characterized by a very intense broad band at ca.  $3450 \text{ cm}^{-1}$  with a poorly resolved shoulder at ca.  $3600 \text{ cm}^{-1}$  which can be attributed to the hydroxyl groups in the supercages and in the sodalite cages respectively [40,41]. In the low energy region the spectrum showed a band at  $1640 \text{ cm}^{-1}$  characteristic of  $\delta(\text{H}_2\text{O})$  mode of absorbed water [42]. The band at ca.  $1020 \text{ cm}^{-1}$  is usually attributed to the asymmetric stretching of Al–O–Si chain of zeolite. The symmetric stretching and bending frequency bands of Al–O–Si framework of zeolite appear at ca. 727 and 513 cm<sup>-1</sup>, respectively [43].

The FTIR spectra of  $Mn(dtta)-Y_A$  and  $Mn(dtta)-Y_B$  are dominated by the strong bands attributed to the zeolite structure. No shift or broadening of the zeolite vibration bands is observed upon encapsulation of the complex. This provides further evidence that the zeolite structure remains unchanged after the encapsulation methods.

In addition to these strong bands originating from the zeolite, the FTIR spectra of the catalysts show the bands in the 1600–1200 cm<sup>-1</sup> region where NaY does not absorb and they are attributed to the presence of the complex. These bands have frequencies that are close to those of the free complex: 1473 and 1400 cm<sup>-1</sup>. Also, in the high energy region, Mn(dtta)-Y<sub>A</sub> and Mn(dtta)-Y<sub>B</sub> catalysts show bands unequivocally assigned to the encapsulated complex at 2690, 2740, 2800 and 2995 cm<sup>-1</sup>. The presence of these bands at frequencies different from those of the free complex, suggests that the manganese complex has a different coordination sphere. This may be a consequence of the physical constraints imposed by the host and due to the host–guest interactions with NaY framework as observed for copper(II) complexes entrapped in NaY [1,23] and NaBEA zeolite [44].

Preservation of NaY zeolite structure of the catalysts was monitored by X-ray powder diffraction. XRD patterns of NaY, and Mn(dtta)-Y<sub>A</sub> and Mn(dtta)-Y<sub>B</sub> catalysts were recorded at  $2\theta$  values between 5° and 65° (Fig. 2).

All catalysts exhibit the typical and similar pattern of highly crystalline Y zeolite. XRD patterns of Mn(dtta)-Y<sub>A</sub> and Mn(dtta)-Y<sub>B</sub> present over 80% of crystallinity. A clear change occurred in the relative peak intensities of 331, 311 and 220 upon introducing the Mn{bis(*p*-tolyl)triazenido} complex. In the case of NaY, the order of peak intensity was found:  $I_{331} > I_{220} > I_{311}$ , while in both heterogeneous catalysts, the order of peak intensity became  $I_{331} > I_{210}$ . This can be attributed to a redistribution of intra zeolite charge balancing cations [45]. These observations indicate that under encapsulation conditions, the synthesis of the complex by different methods has a minor impact on the crystallinity of the zeolite host [46].

Chemical analyses of the catalyst samples were carried out and summarized in Table 1.

The Mn/N ratio was found to be 1.63 and 2.04, for Mn(dtta)- $Y_A$  and Mn(dtta)- $Y_B$ , respectively. Both ratios are much higher than



Scheme 2. Schematic representation of the methods used to encapsulate Mn(dtta) complex in NaY.



Fig. 1. FTIR spectra of free complex (1), catalysts with encapsulated complex,  $Mn(dtta)-Y_A(2)$  and  $Mn(dtta)-Y_B(3)$ , in the ranges: (A) 4000–500 cm<sup>-1</sup> and (B) 1850–500 cm<sup>-1</sup>; in both spectra, correspond to the FTIR spectrum of NaY (4).



Fig. 2. Powder XRD patterns of: (a) NaY, (b) Mn(dtta)-Y<sub>A</sub> and (c) Mn(dtta)-Y<sub>B</sub>.

the theoretical Mn/N ratio, determined for the free complex synthesized (Mn:dtta:Cl is 1:2:1). On the other hand, based on theoretical values of C (48.03%), H (4.30%), N (12.00%) and Mn (15.69%) for [MnCl<sub>2</sub>(dtta)] molecule (Mn:dtta:Cl is 1:1:2), the theoretical Mn/N ratio is 1.31, suggesting that the confined Mn complex in zeolite forms a Mn/ligand complex with a 1:1 stoichiometry. However, for both catalysts, the presence of noncoordinated manganese species was also observed.

X-ray photoelectron spectroscopy experiments were performed in Mn(dtta)-Y<sub>B</sub> catalyst. Low resolution XPS spectrum shows the presence of oxygen, silicon, aluminium and sodium from NaY zeolite. However, the high resolution XPS spectrum shows bands in Si 2p region at 102.88 eV, in Al 2p region at 74.72 eV and in O 1s region at 532.56 eV corresponding respectively to silicon (typical for Si atoms with different chemical environments, such as SiO<sub>4</sub> and terminal Si–OH groups), aluminium (from the tetrahedral AlO<sub>4</sub> groups), oxygen from zeolite framework and a band centred at 1071.0 eV in the Na 1s region corresponding to sodium located in the zeolite matrix [47]. Apart from these features, a single peak is observed in N 1s region at 400.5 eV. This peak position indicates that nitrogen atoms (from the ligand) are coordinated to the metal centre involving sp<sup>2</sup> N donors [48].

In Mn 2p region the high resolution XPS spectrum exhibits different peaks: two main peaks centred at 642.40 and 646.20 eV in the Mn  $2p_{3/2}$ , and 654.13 and 658.07 eV in the Mn  $2p_{1/2}$ . These values are related to two different Mn species presence in the zeolite in agreement with chemical analysis. Moreover, elemental sulfur was also detected (BE = 169.5 eV), suggesting that the SO<sub>4</sub><sup>2–</sup> ions are adsorbed on the surface of the zeolite as the values were close to the detection limit for elemental analysis, i.e. less than 0.01%.

Table 1
Chemical composition of free manganese complex and catalysts obtained.

Sample	С	Н	Ν	Mn <sup>a</sup>	Mn/N
[MnCl(dtta) <sub>2</sub> ]	62.27(62.34) <sup>b</sup>	5.18(5.24) <sup>b</sup>	16.02(15.59) <sup>b</sup>	ND <sup>c</sup> (10.19) <sup>b</sup>	$-(0.65)^{b}$
Mn-Y	ND <sup>c</sup>	ND	ND	1.20 (218.42)	-
Mn(dtta)-Y <sub>A</sub>	0.87	ND	0.22	0.36 (65.53)	1.63
Mn(dtta)-Y <sub>B</sub>	2.23	ND	0.54	1.10 (200.22)	2.04

<sup>a</sup> Obtained from ICP, values in parenthesis total manganese loading in  $\mu$ mol/g (loading = %ICP/(M<sub>Mn[µmol]</sub> × 100%)).

<sup>b</sup> Theoretical values.

<sup>c</sup> ND, not determined.

The combined results from all the techniques used show that the manganese complex encapsulated in zeolite supercages by different methods has a different sphere of coordination from the free complex. These results indicate that manganese is coordinated by one bidentate dtta ligand and the other coordination sites are occupied by water molecule and zeolite framework oxygen [5,22–26,31–33].

#### 3.2. Catalytic activity

The catalytic activity of the heterogeneous catalysts was evaluated by oxidation of styrene and cyclohexanol using acetonitrile as solvent in the presence of *t*BuOOH (oxygen source). The blank experiments were also carried out under the same conditions. The catalytic behaviour of the homogeneous phase was not performed (using free complex as catalysts). As a result, the metal coordination mode in the free complex is different from that of the encapsulated catalyst and this makes it difficult to compare directly the catalytic activities in homogeneous and heterogeneous phases.

Table 2 summarizes the catalytic results for the oxidation of styrene (under optimized conditions). NaY and Mn-Y catalysts (entries 1 and 2) are almost inactive and the benzaldehyde is the major oxidation product. The high benzaldehyde selectivity observed suggests that the acidic nature of zeolite matrix plays a role and leads to epoxide ring opening.

It is clear that the catalytic activities improved in the presence of the encapsulated Mn complex (entries 3 and 5) prepared by two different encapsulation methods. As expected, when the coordination mode changes from oxygen (Mn-Y) to the nitrogen atoms from dtta ligand (Mn(dtta)- $Y_{A/B}$ ) the catalytic activities of the encapsulated complex are enhanced. This may be due to electronic changes induced in the metal centre upon dtta complexation. The enhanced activity of encapsulated catalysts may also be due to the synergy between the catalytic behaviour of the metal complexes and the zeolite host.

The increase in styrene conversion resulted from the presence of the Mn complex by a factor of 9.8 and 8.0 for  $Mn(dtta)-Y_A$  (entry

## Table 3 Oxidation of cyclohexanol catalysed by heterogenized Mn{(1,3-bis(p-tolyl)triazeni-do)} complex in the presence of tBuOOH.

Substrate	Entry	Catalyst	Run	$t(h)^{a}$	%C <sup>b,c</sup>	Cyclohexanone		Cyclohexanone		Cyclohexanone	
						%S <sup>b,d</sup>	%η <sup>b,e</sup>				
OH	7	NaY	1	48	3	100	3				
$\downarrow$	8	Mn-Y	1	48	6	100	6				
	9	Mn(dtta)-Y <sub>A</sub>	1	2	44	100	44				
	10		2	2	4	100	4				
~	11	Mn(dtta)-Y <sub>B</sub>	1	6	1	-	-				

<sup>a</sup> Reaction time at which the substrate conversion start become constant.

<sup>b</sup> Determined by GC against internal standard.

<sup>c</sup> Cyclohexanol conversion (%*C*) calculated as %*C* = {[*A*(cyclohexanol)/*A*(chlorobenzene)]<sub>t = 0 h</sub> × [*A*(cyclohexanol)/*A*(chlorobenzene)]<sub>t = x h</sub>} × 100/[*A*(cyclohexanol)/*A*(chlorobenzene)]<sub>t = 0 h</sub>.

<sup>d</sup> Product selectivity (%S) calculated as %S =  $A(\text{product}) \times 100/[A(\text{product}) + \sum A(\text{other reaction products})].$ 

<sup>e</sup> Product yield ( $\%\eta$ ) calculated as  $\%\eta = \%C \times \%S/100$ ; where A stands for chromatographic peak area.

3) and Mn(dtta)-Y<sub>B</sub> (entry 5), respectively. Both catalysts lead to similar styrene conversion. The conversion decreases slightly in the second reaction cycle for both catalysts (entries 4 and 6).  $Mn(dtta)-Y_A$  (entry 4), shows the highest styrene oxide selectivity in the first catalytic cycle. Nevertheless, a substantial decrease styrene oxide yield is observed for Mn(dtta)-Y<sub>A</sub>. This may be due to some catalyst deactivation and/or manganese complex leaching into reaction media during the first run. However, for Mn(dtta)- $Y_{\rm B}$  (entry 6), both catalytic cycles present the same oxidation product. The decrease in the substrate conversion, usually observed upon immobilization of molecular catalysts into porous supports, may be a consequence of various factors including diffusion restrictions of the substrate through the porous structure of the support and the electronic changes induced in the metal centre through the chemical modifications of the ligands/metal centre as a consequence of the immobilization procedures used [49,50].

However, the catalysts show different activity in cyclohexanol oxidation. The catalytic results obtained for cyclohexanol oxidation, under optimized conditions, are summarized in Table 3.

#### Table 2

Oxidation of styrene catalysed by heterogenized  $Mn\{(1,3-bis(p-tolyl)triazenido)\}$  complex in the presence of tBuOOH.

Substrate	Entry	Catalyst	Run	<i>t</i> (h) <sup>a</sup>	%C <sup>b,c</sup>	Styrene oxide		Benzaldehyde	
						%S <sup>b,d</sup>	$\%\eta^{b,e}$	$S^{b,d}$	%η <sup>ь,е</sup>
1	1	NaY	1	48	4	0	0	100	4
	2	Mn-Y	1	48	9	0	0	100	9
	3	Mn(dtta)-Y <sub>A</sub>	1	48	39	45	18	55	21
	4		2	48	36	14	5	86	31
$\sim$	5	Mn(dtta)-Y <sub>B</sub>	1	48	32	38	12	62	20
	6		2	48	29	38	11	62	18

<sup>a</sup> Reaction time at which the substrate conversion start become constant.

<sup>b</sup> Determined by GC against internal standard.

<sup>c</sup> Styrene conversion (%C) calculated as %C = { $[A(styrene)/A(chlorobenzene)]_{t = 0 h} \times [A(styrene)/A(chlorobenzene)]_{t = x h} \times 100/[A(styrene)/A(chlorobenzene)]_{t = 0 h}$ 

<sup>d</sup> Product selectivity (%S) calculated as %S =  $A(\text{product}) \times 100/[A(\text{product}) + \sum A(\text{other reaction products})]$ .

<sup>e</sup> Product yield ( $\%\eta$ ) calculated as  $\%\eta = \%C \times \%S/100$ ; where A stands for chromatographic peak area.



**Fig. 3.** FTIR spectra of the catalysts (1)  $Mn(dtta)-Y_A$  – as prepared, (2) entry 4, (3) entry 9, (4)  $Mn(dtta)-Y_B$  – as prepared, (5) entry 5 and (6) entry 11; for abbreviation see Tables 2 and 3 in the ranges (A) 4000–500 cm<sup>-1</sup> and (B) 1850–500 cm<sup>-1</sup>.

NaY catalyst presents low catalytic activity (entry 7). Mn-Y catalyst, NaY loaded with manganese(II) sulphate (entry 8), leads to low cyclohexanol conversion. Mn(dtta)-Y<sub>A</sub> catalyst exhibit catalytic activity in the 1st cycle (entry 9) but during their re-use a drastic reduction (40% lower than initial) of cyclohexanol conversion and cyclohexanone yield was observed at the end of the 2nd cycle (entry 10). Mn(dtta)-Y<sub>B</sub> catalyst is almost inactive and leads to negligible substrate conversion (entry 11). This experiment was duplicated and the results were found to be reproducible with a maximum error of ca. 1% relatively to the substrate conversion average. As a consequence of the obtained %C values, Mn(dtta)-Y<sub>A</sub> catalyst was re-used only once, whereas Mn(dtta)-Y<sub>B</sub> was not recycled. The low conversion of cyclohexanol, when Mn(dtta)-Y<sub>B</sub> was used as catalyst, could be related with the sulphate species adsorbed in external surface. These species restrict the access of the substrate and the tBuOOH to active Mn(III)-dtta complex. This result is supported by XPS of Mn(dtta)-Y<sub>B</sub> where the presence of sulphate species is clearly showed. The sulphate species can interact with hydroxyl group from cyclohexanol. This fact is reported in literature where similar behaviour was observed for alcohols [51].

In order to get more insights into the recycled catalysts, FTIR spectra were obtained and depicted in Fig. 3. After catalytic oxidation of cyclohexanol in the presence of  $Mn(dtta)-Y_A$  some band broadening is observed in the frequency range where the vibration bands for the complex occur (Fig. 3 B).

The results indicate that some complex leaches into the reaction medium and/or some degradation of the complex under catalytic reaction conditions occur. This might explain the substantial reduction in cyclohexanone yield in the second reaction cycle (entry 10). For both heterogeneous catalysts studied, FTIR spectra in the range typical for the zeolite matrix do not show significant changes after the catalytic reaction. This suggests that no structural changes took place to the host during the catalytic reaction.

#### 4. Conclusions

Different encapsulation methods were used for the preparation of new heterogeneous catalysts based on  $Mn\{(1,3-bis(p-tolyl)tria-zenido)\}$  complexes in NaY zeolite. Both methods lead to physical

entrapment of manganese complexes without changes in the zeolite framework. Analysis of the data shows that the Mn ion is coordinated by the nitrogen atoms of the bis(*p*-tolyl)triazenido ligand in the host structure with a stoichiometry of 1:1. The other sites in the metal centre are supplied by the zeolite and water molecule inside NaY. Both heterogeneous catalysts showed similar styrene conversion and moderate styrene oxide selectivity. Mn(dtta)-Y<sub>B</sub> can be reused almost without a decrease in its catalytic activity. In contrast, the Mn(dtta)-Y<sub>B</sub> catalyst was not active in oxidation of cyclohexanol.

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