New Mn(II) and Cu(II) chiral C$_2$-multidentate complexes immobilised in zeolites (USY, MCM41) Reusable catalysts for selective oxidation reactions

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Abstract

Heterogenisation of the manganese(II) and copper(II) complexes bearing a triethoxysilyl group on zeolites (modified ultrastable Y zeolite (USY), MCM-41) through covalent bonding to support and the preparation of the respective Mn-complex encapsulated into the supercages of large pore sized Y zeolite are reported. The chemical environment of the metal in these materials does not change after heterogenisation as we confirm by FT-IR, diffuse reflectance and thermogravimetric (TG) analysis. All catalysts, homogeneous and heterogenised, are active and selective in the oxidation of alkyl phenyl sulfides and nerol at low temperatures using sodium hypochlorite or IOPh as terminal oxidant. The catalytic activity of the anchored USY and MCM41 complexes is higher than the corresponding homogeneous or encapsulated ones, yielding sulfoxides and epoxyalcohols with excellent yields and selectivity and moderate enantioselectivity. Life time of heterogenised catalysts has been examined by repeated use of the complexes leading similar rates and yields of sulfoxide or epoxide, whilst no appreciable loss of metal has been observed over several runs.
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Keywords: Manganese; Copper; Heterogenised; Encapsulated; Sulfide; Oxidation; Epoxidation

1. Introduction

The use of chiral catalysts has become a powerful methodology in modern synthetic organic chemistry [1]. As far as oxygen-transfer catalysis is concerned, the Sharpless–Katsuki epoxidation of allylic alcohols constituted an authentic breakthrough in this field [2,3]. More recently, Jacobsen and co-workers expanded the scope of the catalytic asymmetric epoxidation to some families of unfunctionalised alkenes with high stereocontrol by using chiral (salen) Mn complexes [4]. The recent results of Bonchio et al. [5] shows the state-of-the-art for sulfoxidation catalysts (based on Ti, Zr).

In the last decade, much effort has been paid to immobilise these homogeneous catalysts onto solid supports because such heterogenisation of homogeneous catalysts may combine the ease of product separation with the selectivity founded with homogeneous complexes [6]. For manganese three approaches have been adopted: (i) supporting Mn epoxidation catalysts on polymers [7] or zeolites [8]; (ii) ion exchange of manganese complexes into the intra-crystalline space of zeolites, e.g. zeolite Y [9] or mesoporous materials [10]; and (iii) encapsulation of manganese complexes

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within zeolites by synthesis using "ship-in-a-bottle" methodology [11,12].

Zeolites are crystalline aluminosilicates whose internal voids are formed by cavities and channels of strictly regular dimensions and of different sizes and shapes. In particular, the pore structure of Y zeolite consists of almost spherical 13 Å cavities interconnected tetrahedrally through smaller apertures of 7.4 Å diameter. The metal complex can be easily accommodated inside the supercages of Y zeolite. Also, there is now considerable interest in the application of the new generation of mesoporous siliceous and non-siliceous oxides as catalyst support materials. MCM-41 is one member of this family [13]. The inner surfaces of MCM-41 are covered with nucleophilic silanols, which enable the immobilisation of transition metals catalysts by directing grafting with transition metal complexes.

The use as chiral catalysts of Mn(II)-complexes heterogenised on or embedded within zeolite opens a new methodology that allows a wide variety of reaction conditions while diminishes the deactivating process owing to Mn dimerisation. Furthermore, on top of the enantioselectivity the overall process would benefit of the shape-selectivity characteristic of the zeolite catalysis.

Although the heterogenisation strategy has been well stabilised in oxidation processes [14] in the present contribution, we report our results on the synthesis and characterisation of a series of Mn(II) and Cu(II)-complexes with multidentate C_2-symmetry ligands derived from L-proline and the heterogenisation of such complexes by anchoring (on ultrastable Y zeolite (USY) and MCM-41 zeolites) or encapsulating into the supercages of large pore sized USY zeolite. The oxidation properties of all synthesised complexes are studied making special attention on the role of the support on the activity and selectivity of catalysts. Thus, the heterogenised complex gives higher catalytic activity for oxidation reactions than its solution counterpart and showed no significant loss of catalytic activity when recycled.

2. Experimental

The silylating agent N-(2-aminoethyl-3-aminopropyl)triethoxysilane was obtained as described in the literature [15]. C, H and N analyses were carried out by the Analytical Department of the Institute of Materials Science (CSIC) with a Perkin-Elmer 240C apparatus. Metal contents were analysed by atomic absorption using a Unicam Philips SP9 apparatus. IR spectra were recorded with a Nicolet XR60 spectrophotometer (range 4000–200 cm^{-1}) as KBr pellets. Gas chromatography (GC) analysis was performed using a Hewlett-Packard 5890 II with a flame ionisation detector in a cross-linked methylsilicone column.

The inorganic support for anchoring were a modified USY and a mesoporous MCM-41. USY zeolite was prepared by steam calcination at 1023 K of an 80% ammonium-exchanged NaY (SK40 Union Carbide), followed by treatment with a 1N citric acid solution at 333 K for 30 min to remove extra-framework species. After this, the zeolite was thoroughly washed and dried at 403 K for 6 h. The final zeolite had a well-developed supermicropore–mesopore system (pore diameter 12–30 Å besides the typical ca. 12 Å micropores). The controlled dealumination promotes destruction of some sodalite units, which allowed direct communication between α-cages generating cavities wider than 12 Å. The formation of supermicropores and large mesopores has been detected by N_2 adsorption–desorption. The main characteristics of the resultant zeolite are: unit cell size, 24.40 Å; bulk SiO_2/Al_2O_3, 4.2; crystallinity, >95%. A detailed synthesis procedure for purely siliceous MCM-41 has been described [14]. MnY zeolite was prepared starting from NaY by ion exchange using a 5 mM aqueous solution of $Mn(CH_3COO)_2$ and 1–10 solid-to-liquid weight ratio. The resulting MnY zeolite containing 1.6 Mn^{2+} ions per unit cell (which corresponds to an average of 1 Mn^{2+} every five supercages) was filtered, washed with deionised water and air-dried at 100 °C for 48 h. The inorganic supports were dried at 415 K under 0.01 Torr for 2 h, before the heterogenisation process. This treatment is sufficient to achieve complete thermodesorption of physically absorbed water molecules from the surface.

2.1. Synthesis of ligands

The ligands N,N′-bis[(S)-prolyl]ethylenediamine (**1a**), N,N′-bis[(S)-prolyl]-N-(2-aminoethyl-3-aminopropyl)triethoxysilylethylenediamine (**1b**), N,N′-bis-[(S)-N-benzylprolyl]ethylenediamine (**2a**), N,N′-bis-
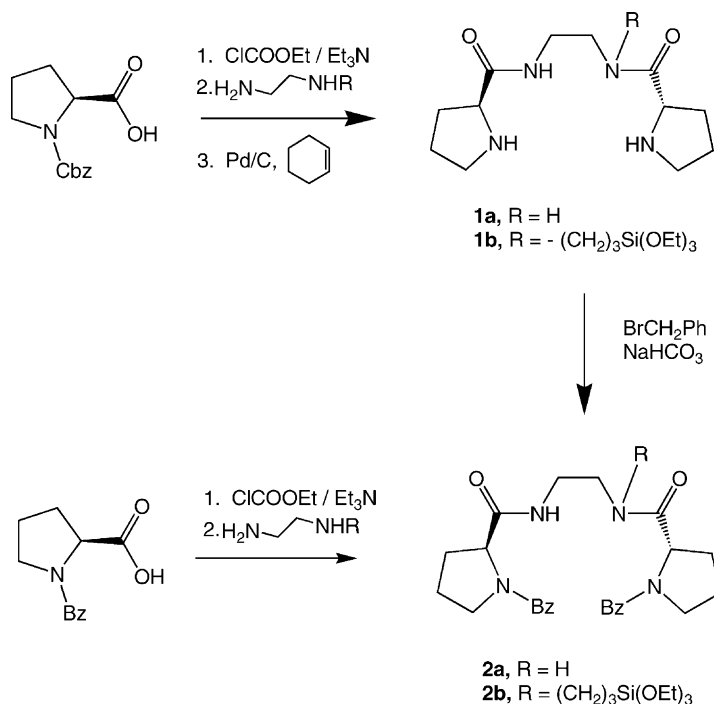
Scheme 1. Synthesis of ligands.

[(S)-benzylprolyl]-N-(2-aminoethyl-3-aminopropyl) triethoxysilylethylenediamine (**2b**) were synthesised recently in our laboratory [16] see Scheme 1.

2.2. Synthesis of complexes

2.2.1. Synthesis of manganese complexes

General method: To a solution of ligand **1–2a,b** (1 mmol) in ethanol (30 cm^3) was added MnCl$_2$·4H$_2$O (198 mg, 1 mmol) and NH$_4$PF$_6$ (162 mg, 1 mmol) and the mixture was refluxed for 3 h. The precipitated white product was filtered and the filtrate was concentrated by rotary evaporation to give more of the white solid. The combined solids were washed with small portions of ethanol and then dried in vacuo.

2.2.1.1. [Mn(N,N′-bis[(S)-prolyl-N-(2-aminoethyl-3-aminopropyl)triethoxysilyl]ethylenediamine)Cl] PF$_6$. [Mn(**1b**)Cl]PF$_6$: Yield: 55%. mp > 230 °C. C$_{17}$H$_{34}$ClF$_6$MnN$_4$O$_5$PSi (638): calc. (with Si(OCH$_2$-CH$_3$)$_3$ as Si(OCH$_2$CH$_3$)(OH)$_2$): C 32.0; H 5.4; N 8.8; Mn 8.6. found C 31.7; H 5.1; N 8.6; Mn 8.9%. IR (KBr, cm^{-1}): ν = 3410 (N–H); 1680, 1630 (C=O); 1560

(N–C=O); 1120 (C–Si); 850 (P–F). UV-Vis (10^{-3} M, DMF): λ nm (log ϵ) = 285.5 (2.4). TG analysis: 0.584 mg weight loss (12.4% of 4.68 mg complex; expected weight loss 12.7%) at 93–108 °C (EtOH + 2H$_2$O).

2.2.1.2. [Mn(N,N′-bis[(S)-benzylprolyl]-N-(2-aminoethyl-3-aminopropyl)triethoxysilyl]ethylene-diamine)Cl(H$_2$O)]PF$_6$. [Mn(**2b**)Cl(H$_2$O)]PF$_6$: Yield: 55%. mp > 203 °C (d). Λ_M (10^{-3} M, Ω^{-1} cm^2 mol^{-1}, CH$_3$CN) = 143–145 C$_{35}$H$_{56}$ClF$_6$MnN$_4$O$_6$PSi (892): calc.: C 47.1; H 6.3; N 6.3; Mn 6.1. found C 47.5; H 6.0; N 6.0; Mn 6.4%. UV-Vis (10^{-3} M, DMF): λ nm (log ϵ) = 285.7 (2.7). IR (KBr, cm^{-1}): ν = 3542 (OH); 3392 (N–H); 1636 (C=O), 1611 (N–C=O); 1071 (C–Si); 836 (P–F). MS$^+$(m/z): 915 ([MnCl(**2b**)(CH$_3$CN)]PF$_6$; 729 ([MnCl(**2b**)]$^+$. TG analysis: 0.520 mg weight loss (11.8% of 4.42 mg complex; expected weight loss 11.4%) at 95–118 °C.

2.2.2. Synthesis of copper complexes

General: to a solution of [Cu(CH$_3$CN)$_4$]ClO$_4$ (1 mmol) in dry acetonitrile (20 ml) was added a

solution of the corresponding ligand **1–2a,b** (1 mmol); the mixture was stirred for 3 h at room temperature and the crystalline precipitate filtered. The filtrate was evaporated under reduced pressure to a volume of 5 ml and a careful addition of diethyl ether caused the precipitation of a microcrystalline blue solid, which was collected by filtration, washed and dried in vacuo (10^{-3} mm Hg/8 h) to give the desired complex.

2.2.2.1. [Cu(N,N'-bis[(S)-prolyl-N-(2-aminoethyl-3-aminopropyl)triethoxysilyl]ethylenediamine)]ClO₄.

[Cu(**1b**)]ClO₄·2H₂O: Yield: 66%. mp = 225–230 °C. Λ_M (10^{-3} M, Ω^{-1} cm^2 mol^{-1}, CH₃CN) = 154–168. $C_{15}H_{34}ClCuN_4O_{11}Si$ (574): calc. (with Si(OCH₂-CH₃)₃ as Si(OH)₃): C 31.4; H 6.0; N 9.8; Cu 11.1. found C 31.1; H 5.8; N 10.0; Cu 11.4%. UV-Vis (10^{-3} M, DMF): λ nm (log ϵ) = 637.5 (w); 290.0 (3.5). IR (KBr, cm^{-1}): ν = 3460, 3300 (N–H); 1680 (C=O), 1620; 1590 (N–C=O); 1100 (C–Si); 1080 (Cl–O). TG analysis: 0.820 mg weight loss (18.98% of 4.32 mg complex; expected weight loss 19.5%) at 95–113 °C (5H₂O).

2.2.2.2. [Cu(acetonitrile)(N,N'-bis[(S)-benzylprolyl]-N-(2-aminoethyl-3-aminopropyl)triethoxysilyl]-ethylenediamine)]ClO₄.

[Cu(**2b**)(CH₃CN)]ClO₄: Yield: 56%. mp > 250 °C. Λ_M (10^{-3} M, Ω^{-1} cm^2 mol^{-1}, CH₃CN) = 122–125. $C_{37}H_{57}ClCuN_5O_9Si$ (843): calc.: C 52.7; H 6.8; N 8.3; Cu 7.5. found C 52.3 H 6.8; N 8.0; Cu 7.4%. UV-Vis (10^{-3} M, DMF): λ nm (log ϵ) = 355.5 (2.43); 288.50 (3.5). IR (KBr, cm^{-1}): ν = 3772, 3542 (OH); 3300 (N–H); 1670 (C=O), 1621; 1592 (N–C=O); 1100 (C–Si); 1090 (Cl–O). MS$^+$(m/z): 742 [Cu(**2b**)(CH₃CN)]$^+$, 700 [Cu(**2b**)]$^+$. TG analysis: 0.660 mg weight loss (14.8% of 4.60 mg complex; expected weight loss 14.8%) at 102–126 °C.

The manganese and copper complexes for homogeneous catalysis, used as reference, were obtained as we have previously described [17].

2.3. Heterogenisation of M(II) complexes

2.3.1. Anchoring on USY and MCM-41-zeolite

The zeolite-M(II)-complexes were prepared as we have previously described [18,19]. Thus, a solution of the silyl-complex, (0.5 mmol) in ethanol (Mn-complexes) or acetonitrile (Cu-complexes; 2 ml) was added to a well-stirred toluene suspension (40 ml) of the inorganic support (modified USY-zeolite or MCM-41 dried at 140 °C/0.1 mm/Hg for 3–4 h, 1 g) and the mixture was stirred at room temperature for 24 h. The solid was then filtered and Soxhlet extracted with acetonitrile-ethyl ether, EtOH-ethyl ether (1:2) for 7–24 h to remove the remaining non-supported complex from heterogenised catalyst. The resulting white solid was dried in vacuo and analysed.

USY Mn1b: Elemental analysis indicated 0.41 mass% Mn. IR (KBr, cm^{-1}): ν = 3400 (N–H); 1670, 1620 (C=O); 1233 (vs, support); 1120 (C–Si); 1083 (vs, support); 848 (P–F). UV-Vis (solid; nm): 305.

MCM-Mn1b: Elemental analysis indicated 0.43 mass% Mn. IR (KBr, cm^{-1}): ν = 3400 (N–H); 1670, 1620 (C=O); 1233 (vs, support); 1120 (C–Si); 1083 (vs, support); 848 (P–F). UV-Vis (solid; nm): 299.

MCM-Mn2b: Elemental analysis indicated 0.39 mass% Mn. IR (KBr, cm^{-1}): ν = 3380–3300 (O–H, N–H); 1670, 1659 (C=O); 1237 (vs, support); 1100–1083 (C–Si, support); 840 (P–F). UV-Vis (solid; nm): 300.

USY-Cu1b: Elemental analysis indicated 0.86 mass% Cu. IR (KBr, cm^{-1}): ν = 3440–3300 (N-H); 1670, 1600 (C=O); 1236 (vs, support); 1100–1083 (C–Si, support); 1000 (Cl–O). UV-Vis (solid; nm): 598 (w), 300.

MCM-Cu1b: Elemental analysis indicated 0.92 mass% Cu. IR (KBr, cm^{-1}): ν = 3440–3300 (N–H); 1670, 1600 (C=O); 1236 (vs, support); 1100–1083 (C–Si, support); 1000 (Cl–O). UV-Vis (solid; nm): 602 (w), 299.

MCM-Cu2b: Elemental analysis indicated 0.82 mass% Cu. IR (KBr, cm^{-1}): ν = 3440–3300 (O-H, N-H); 1670, 1600 (C=O); 1236 (vs, support); 1100–1083 (C–Si, support, Cl–O). UV-Vis (solid; nm): 356, 310.

2.3.2. Encapsulated complexes on Y zeolite

Complexation of the ligands with MnY was made as follows: thus, thermally dehydrated MnY zeolite (1 g) was poured into a CH₂Cl₂ solution containing the ligand (1 mmol). The resulting suspension was magnetically stirred at reflux temperature for 12 h, filtered and washed exhaustively with CH₂Cl₂. Finally, the white MnY zeolites samples were Soxhlet extracted with CH₂Cl₂ to reduce the presence of unreacted and surface species from the zeolite particles.

Residual uncomplexed MnY can contribute to the catalysis of the oxidation in a non-enantioselective manner. This would diminish the overall enantioselectivity of the system. In order to minimise these undesirable sites, the Mn(II)-zeolites were stirred with aqueous solutions of NaNO$_3$ (0.1 M) to re-exchange uncomplexed manganese ions.

MnY1a: Elemental analysis indicated 1.82 mass% Mn. IR (KBr, cm^{-1}): $\nu = 3410$, 3250 (N–H); 1650, 1620 (C=O); 1234 (vs, support); 1083 (vs, support).

MnY2a: Elemental analysis indicated 1.36 mass% Mn. IR (KBr, cm^{-1}): $\nu = 3420$, 3300 (N–H); 1670 (C=O); 1233 (vs, support); 1083 (vs, support).

2.4. Reactivity: oxidation of sulfides and alkenes catalysed by Mn(II)-complexes

Oxidation reactions were carried out in a 15 ml flask equipped with a magnetic stirrer. The flask was charged with: (i) 3 ml of a solution or suspension of the catalyst (0.01 mmol) in CH$_2$Cl$_2$; (ii) a solution of the substrate (olefin or sulfide, 1 mmol) in CH$_2$Cl$_2$; (iii) 4-methylmorpholine N-oxide monohydrate (0.1 mmol). The mixture was allowed to desired temperature. Subsequently the oxidant [aqueous NaOCl (pH = 11.3, 1.9 mmol), H$_2$O$_2$ (30%; 2.5 mmol) or solid IOPh (2 mmol)] was added and the reaction mixture was stirred. Chemical yields and the enantiomeric excesses of methyl phenyl sulfide and nerol were measured by GC with a chiral glass capillary column (mixture of methylsilicone (OV-1701) and methylsilicone-heptakis-[2,3-dipentyl-6-(*t*-butyldimethylsilyl)]-β-cyclodextrin as stationary phase) [20]. The ee for (2-ethylbutyl) phenyl sulfide was determined by ^{1}H-NMR using (-)-MPPA ((*R*)-(-)-α-methoxyphenylacetic acid) as chiral agent [21].

3. Results and discussion

3.1. Synthesis of complexes

The structures of complexes, characterised analytical and spectroscopically, demonstrate the considerable flexibility in the conformations that multidentate ligands can adopt (Fig. 1). The coordinating solvents have been verified by the appropriate losses in their thermogravimetric (TG) analyses.

3.2. Heterogenisation of complexes

In the era of green chemistry, the heterogenisation of homogeneous catalysts is a field of continuing interest: indeed, although some of these organometallic complexes exhibit remarkable catalytic properties (activities and selectivity), they are unsuitable to separate intact, from the reaction medium making difficult their reuse and contaminating the reaction products. Thus, the heterogenisation is always a toxicological and environmental challenge; moreover it has an economical significance unless the activity of the homogeneous catalysts was exceptionally high. We have considered two strategies for heterogenisation, which preserve as much as possible the coordination sphere of the metal. This is achieved (described in the undermentioned sections).

3.2.1. By anchoring

By anchoring the homogeneous catalyst to an inorganic support (USY or MCM-41 zeolite) via covalent bonds between the solid (silanol groups –Si–OH) and one ligand that have appropriate groups (–Si(OEt)$_3$) at a position remote to the metal center (Scheme 2a). Preparations of these materials were carried out, by controlled hydrolysis of Si–OEt bonds and reaction with the free silanol (Si–OH) on the surface of an USY or MCM-41 zeolite. IR and UV-Vis spectroscopy confirmed the fact that the resulting catalytic material is very stable and the species are covalently bonded to the surface showing only minor frequency shifts from those of the corresponding "neat" complex. The elemental analysis of C, H, N and M also confirm the M/ligand (1:1) stoichiometry. It is unlikely that the nature of the complex is substantially altered under the relatively mild conditions of the anchoring reaction [22]. TG analysis shows that the total weight loss is associated with the metal complex content corresponding to composition of the organic ligands. The loading of metal is always ca. ∼1–2% (±0.1%) measured by atomic absorption of metal of the digested samples These values have been used for calculating the ratio catalyst/substrate in the reaction tests.

3.2.2. By encapsulating

By encapsulating or encaging the catalyst in the voids of a porous inorganic solid (Y zeolite; Scheme 2b).
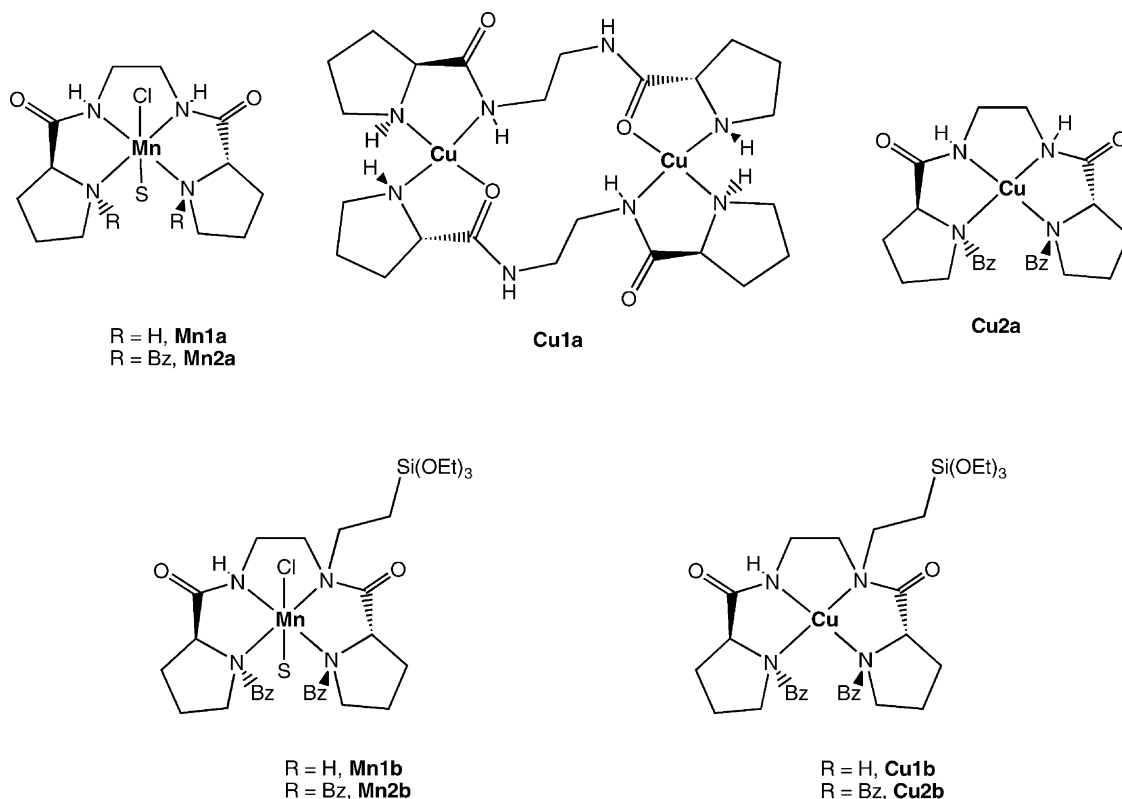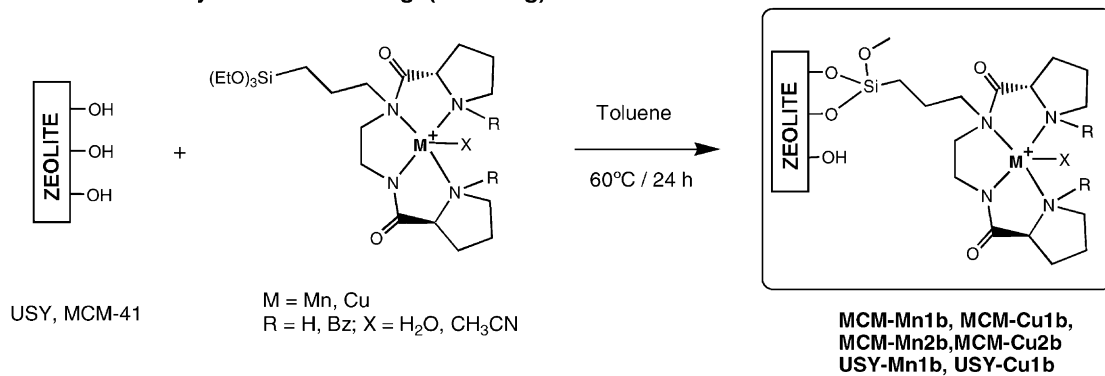
Fig. 1. Structure of new complexes.

The objective, clearly, is to improve the stability of the metal complex under the reaction conditions by preventing the catalytic species from dimerizing or aggregation, and to tune the selectivity of the reaction using the walls of the pores of the solid via steric constraints. In this approach, the metal is introduced in the pores of a solid via cation exchange. The ligands, **1a**–**2a**, are then introduced under the conditions indicated in the experimental section for complex formation. According to the "flexible-ligand" strategy for the encapsulation of metal complexes inside the cavities of zeolite hosts, the free ligands are flexible enough to diffuse through the ring windows into the cavities of zeolite Y, where the metal cations are located. There, complexation occurs and the resulting complexes are too bulky and rigid to be able to leave the cavities again. Uncomplexed ligands and complexes formed at the external surface of the zeolite crystallites have to be removed as far as possible. Identity of the complex has been established by spectroscopic methods

and IR and UV reflectance spectra of encapsulated complexes are coincident with that recorded for homogeneous complexes. The complex formed is like a "ship-in-bottle", confined in the supercages of the zeolite: this explains the greater stability of these catalysts as compared with the same complexes in solution. No metal leaching is observed, as long as the complex is exclusively inside the pores.

IR spectroscopy provides information on the integrity of the anchored and encapsulated complexes, as well as the crystallinity of the host zeolite. The IR bands of all heterogenised complexes are weak due to their low concentration in the zeolite. Metal complexes encapsulated in the zeolite cages did not show any significant shift in NH or C=O stretching modes. We did not notice any appreciable changes in the frequencies of Mn- or Cu-complexes after incorporation into zeolite matrix.
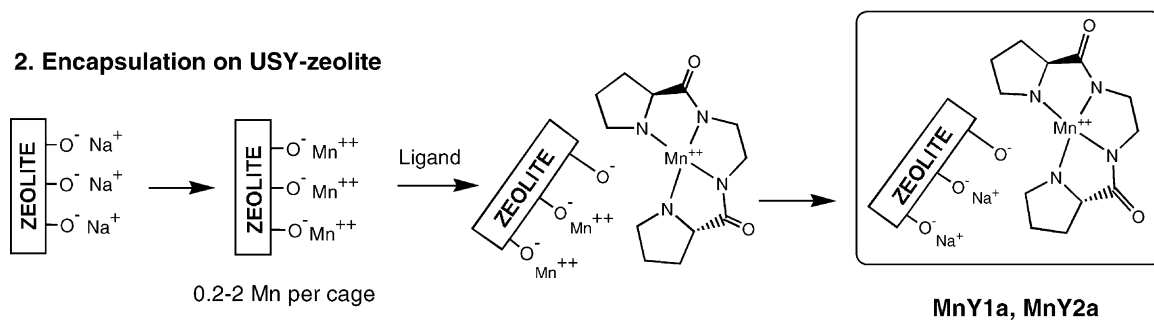
The diffuse reflectance spectra of M (C$_2$-ligand) complexes are almost identical before and after

1. Anchored by covalent bonding (tethering)

USY, MCM-41

M = Mn, Cu
R = H, Bz; X = H_2O, CH_3CN

MCM-Mn1b, MCM-Cu1b,
MCM-Mn2b, MCM-Cu2b
USY-Mn1b, USY-Cu1b

2. Encapsulation on USY-zeolite

0.2-2 Mn per cage

MnY1a, MnY2a

Scheme 2. Preparation of heterogenised complexes: (a) anchored by covalent bond; (b) encapsulated in the supercages of zeolite Y.

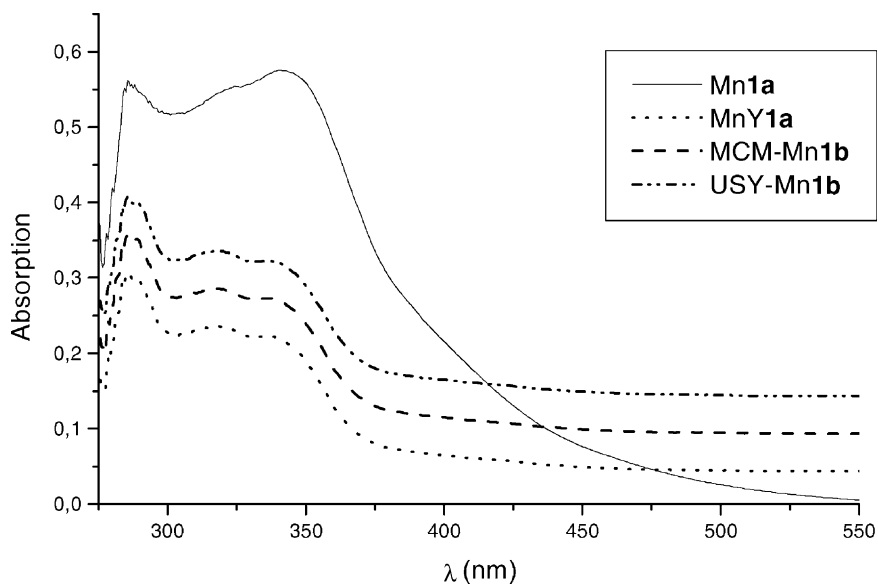Fig. 2. UV-Vis diffuse reflectance spectra of Mn**1a**, MnY**1a**, MCM-Mn**1b** and USY-Mn**1b**.

heterogenisation process (Fig. 2), indicating that the complexes maintain their geometry and their electronic surrounding even after heterogenisation without significant distortion.

4. Reactivity

The new materials were tested in the oxidation of organic substrates, using methyl phenyl sulfide, (2-ethylbutyl) phenyl sulfide and nerol as model substrates. Aqueous sodium hypochlorite (NaOCl), 30% hydrogen peroxide (30% H_2O_2) and iodosylbenzene (PhIO) were employed as primary oxidants, always in excess with respect to the substrate. Reactions were carried out at 0 °C in the case of methyl phenyl sulfide and nerol, and at room temperature with (2-ethylbutyl) phenyl sulfide. Higher reaction temperatures lead to a dramatic decrease in the selectivity to sulfoxide or epoxide as well as a significant loss of the asymmetric induction. If solid IOPh was employed as oxidant, reactions were performed at room temperature. The pH of the aqueous solution of NaOCl was adjusted at 11.3. The outcome of the reactions was followed by GC and results are summarised in Tables 1–4, Figs. 3–10.

The experimental conditions were established by varying the nature of the oxidant. First, hydrogen

peroxide (H_2O_2) was examined as oxidant in acetonitrile and little formation of sulfoxide was detected at ambient temperature in spite of excess amount of oxidant used whilst NaOCl yield high conversions at low temperature. The 4-methylmorpholine N-oxide monohydrate is used to stabilise the Mn(V)=O complex formed in the oxidation cycle. A series of blank experiments revealed that each component is essential for an effective catalytic reaction and the system is relatively unaffected by changing the order of mixing. All heterogenised catalysts appeared to be stable under experimental conditions (as the catalysts recovered by filtration of the reaction mixture and washing with CH_2Cl_2 were found to be reactive for further catalytic runs), but undergo some degradation over extensive use for 48 h as evidenced by some 5–10% loss of metal content.

4.1. Oxidation of alkyl phenyl sulfides

The selective oxidation of sulfides to sulfoxides has been a challenge for many years, partly due to the importance of sulfoxides as intermediates and auxiliaries in organic synthesis [23]. In recent years selective oxidation of sulfides to sulfoxides has been carried out with a large number of heterogeneous and supported reagents [24]. Here, we report our results

Table 1

Oxidation of alkyl phenyl sulfides catalysed by Mn(C_2-symmetry ligands) complexes in homogeneous and heterogenised–homogeneous conditions

Substrate	Catalyst	T (°C)	Conversion % (t)	Selectivity SO (%)[a]	TOF[b]	ee (%)[c]
Methyl phenyl sulfide	**Mn1a**	0	76 (2 h)	67	163	23.2
	MnY**1a**	0	76 (3 h)	31	73	18.8
	USY-Mn**1b**	0	92 (1 h)	57	311	14.2
	MCM-Mn**1b**	0	78 (1 h)	29	274	10.8
	Mn2a	0	75 (2 h)	65	141	16.1
	MnY**2a**	0	73 (3 h)	26	30	10.8
	MCM-Mn**2b**	0	81 (1 h)	68	295	15.3
(2-Ethylbutyl) phenyl sulfide	**Mn1a**	Room temperature	100 (2 h)	69	74	5
	MnY**1a**	Room temperature	95 (1.5 h)	95	213	8.0
	USY-Mn**1b**	Room temperature	100 (20 min)	93	586	5.0
	MCM-Mn**1b**	Room temperature	85 (60 min)	90	505	10.0
	Mn2a	Room temperature	78 (2 h)	73	58	5.2
	MnY**2a**	Room temperature	100 (3.5 h)	86	93	12.0
	MCM-Mn**2b**	Room temperature	100 (3 h)	92	155	13.3

[a] Amount of sulfoxide/amount of sulfide consumed.

[b] TOF: mmol substrate/mmol catalyst min.

[c] ee determined by GC–MS and ^{1}H-NMR.

Table 2

Oxidation of methyl phenyl sulfide catalysed by Mn(C_2-symmetry ligands) complexes in homogeneous and heterogenised–homogeneous conditions using IOPh as oxidant[a]

Substrate	Catalyst	Conversion % (t)[b]	Selectivity SO (%)[c]	TOF[d]	ee (%)[e]
Methyl phenyl sulfide	Mn**1a**	88 (4 h)	96.6	123	26.7
	MCM-Mn**1b**	45 (6 h)	100	30	20.0
	Mn**2a**	78 (4 h)	100	113	39.7
	MCM-Mn**2b**	30 (6 h)	97.7	13	31.8

[a] Reaction performed at room temperature.
[b] Conversion >80 was achieved after 24 h in all cases.
[c] Amount of sulfoxide/amount of sulfide consumed.
[d] TOF: mmol substrate/mmol catalyst min.
[e] ee determined by GC–MS and ^{1}H-NMR.

Table 3

Oxidation of alkylsulfides catalysed by Cu(C_2-symmetry ligands) complexes in homogeneous and heterogenised–homogeneous conditions

Substrate	Catalysis	T (°C)	Conversion % (t)	Selectivity SO (%)[a]	TOF[b]	ee (%)[c]
Methyl phenyl sulfide	Cu**1a**	0	86 (3 h)	51	103	18.5
	USY-Cu**1b**	0	83 (60 min)	57	250	22.5
	MCM-Cu**1b**	0	67 (30 min)	25	225	21.6
(2-Ethylbutyl) phenyl sulfide	Cu**1a**	Room temperature	100 (7 h)	78	22	4
	USY-Cu**1b**	Room temperature	90 (60 min)	92	209	24
	MCM-Cu**1b**	Room temperature	100 (20 min)	93	500	28

[a] Amount of sulfoxide/amount of sulfide consumed.
[b] TOF: mmol substrate/mmol catalyst min.
[c] ee determined by GC–MS and ^{1}H-NMR.

with soluble and heterogenised Mn and Cu complexes (Tables 1–3).

The results given in Figs. 3 and 4 show that for the case of methyl phenyl sulfide the activity is higher for the USY-M**1b** catalyst than for the MCM-M**1b**, MnY**1a** and homogenous. Moreover, the selectivity shows that the sulfoxide is a primary and unstable product, while the corresponding sulfone appears as a secondary and stable product. USY-M**1b** is more selective towards the formation of sulfoxide than MCM-M**1b** and MnY**1a**. The reactions showed a high chemoselectivity for larger (2-ethylbutyl) phenyl sulfide (Fig. 7). Indeed, in most of the cases sulfoxides were obtained as the main or sole products as detected

Table 4

Oxidation of nerol catalysed by Mn(C_2-symmetry ligands) complexes in homogeneous and heterogenised–homogeneous conditions

Catalyst	T (°C)	Conversion % (t)[a]	Selectivity to epoxide 2, 3 (%)[b]	TOF[c]	ee (%)[d]
Mn**1a**	Room temperature	55 (2 h)	56	59	2.4
Mn**1a**	0	52 (8 h)	68	13	3.3
MnY**1a**	0	45 (8 h)	73	11	4.1
USY-Mn**1b**	0	52 (8 h)	60	17	3.0
MCM-Mn**1b**	0	100 (6 h)	46	50	4.2

[a] Conversion total was achieved after 24 h.
[b] Amount of epoxide/amount of alkene consumed.
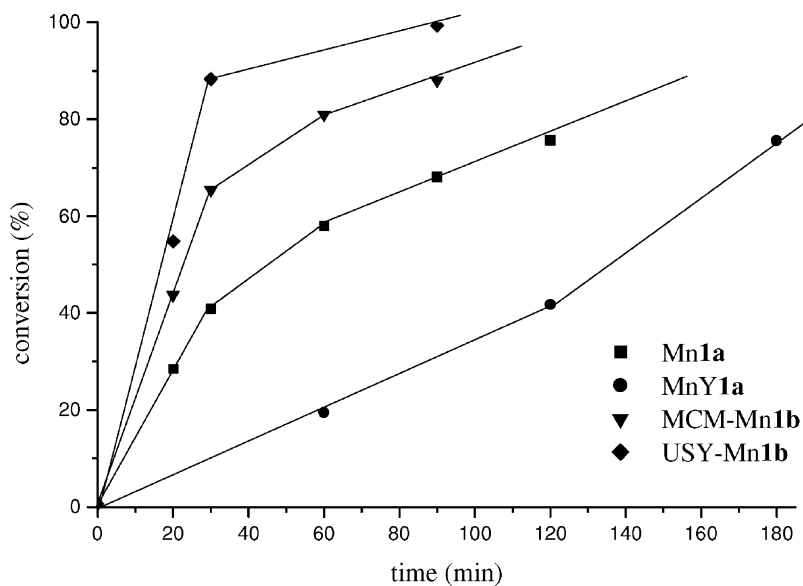[c] TOF: mmol substrate/mmol catalyst min.
[d] ee determined by GC–MS and ^{1}H-NMR.

Fig. 3. Kinetic profile of oxidation of methyl phenyl sulfide with Mn-catalysts ($T = 273$ K).

by GC, TLC and ^{1}H-NMR analysis. Furthermore, products of the oxidation of the (2-ethylbutyl) phenyl sulfide were not detected at 0 °C. The lower selectivity found for methyl phenyl sulfide corresponds with the much higher extent of the reaction with this substrate.

As can be concluded from Table 1, methyl phenyl sulfide and (2-ethylbutyl) phenyl sulfide have shown a quite similar behaviour when the same catalyst was used in their oxidative transformations, suggesting that despite the differences in their structures, they
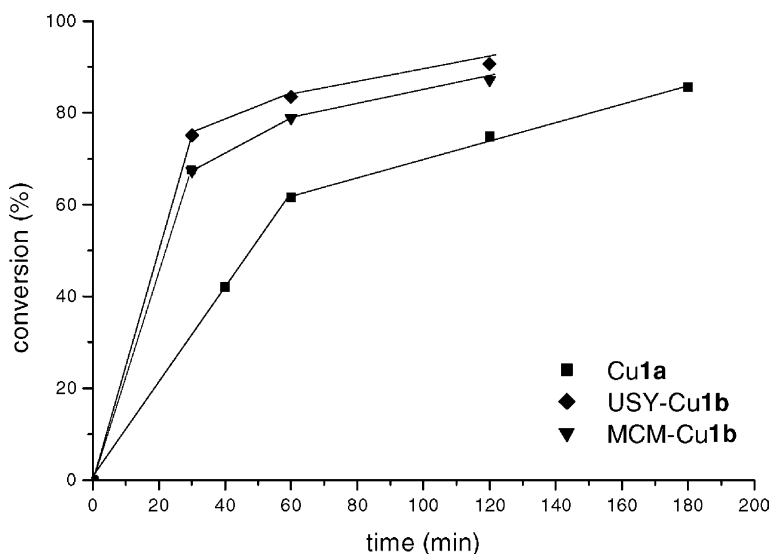
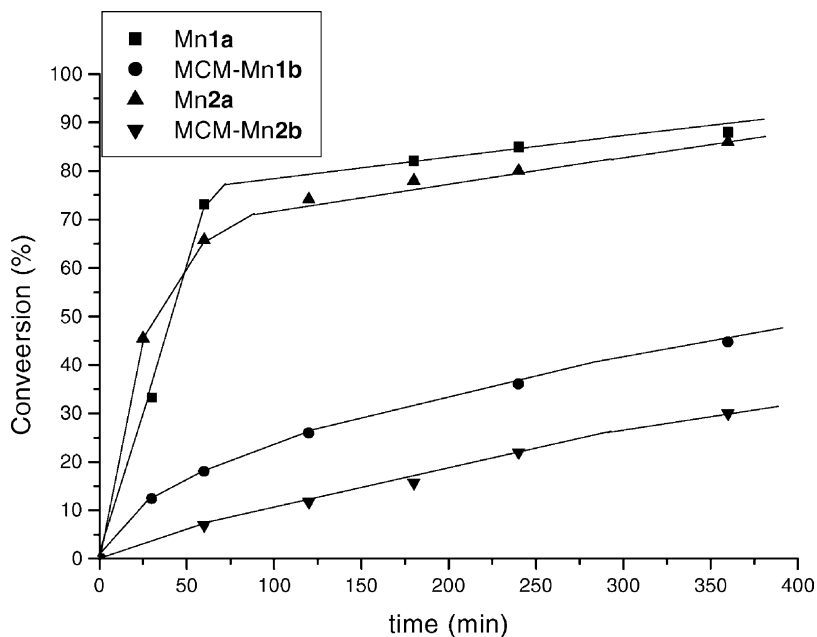Fig. 4. Kinetic profile of oxidation of methyl phenyl sulfide with Cu-catalysts ($T = 273$ K).

Fig. 5. Kinetic profile of oxidation of methyl phenyl sulfide with Mn-catalysts ($T = 293$ K), using IOPh as oxidant (conversion >80 was achieved after 24 h in all cases).
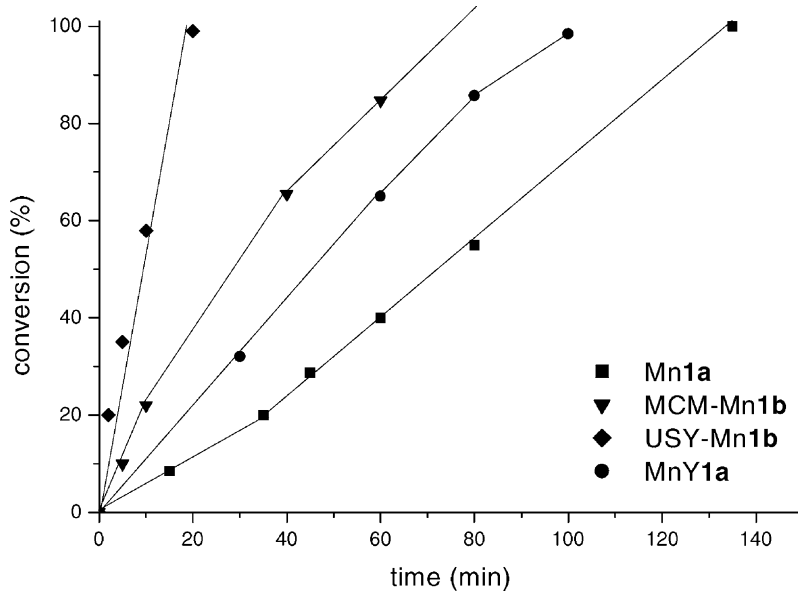

Fig. 6. Kinetic profile of oxidation of (2-ethylbutyl) phenyl sulfide with Mn-catalysts ($T = 293$ K).
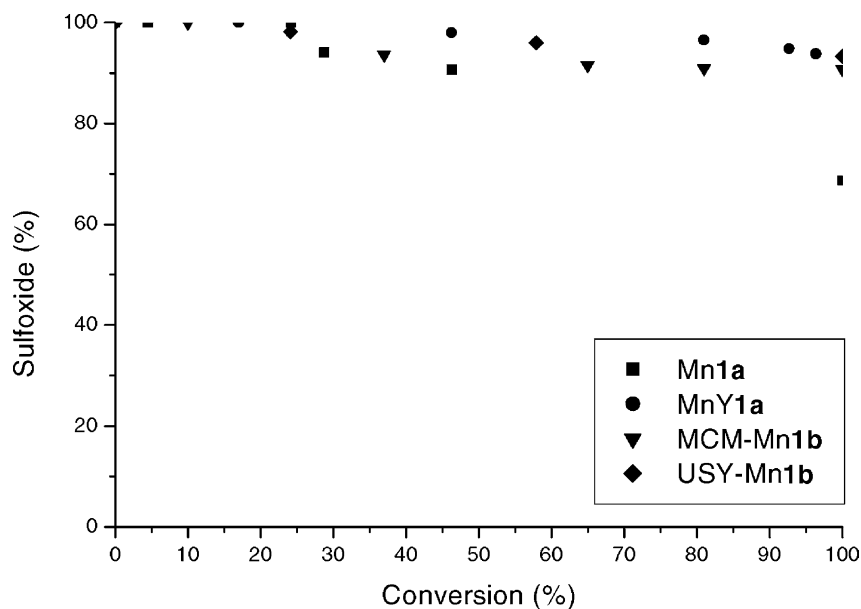
Fig. 7. Selectivity to (2-ethylbutyl) phenyl sulfoxide for the oxidation reactions carried out with Mn-catalysts (homogeneous and heterogenised).

have quite the same reactivity. The copper complexes show less activity (Fig. 4) and similar selectivity that manganese ones. This may be due to the fact that the formation of Cu-oxo species (catalytically ac-

tive intermediate) is kinetically less favoured in this case.

The lower reaction rates obtained for the oxidation of methyl phenyl sulfide with the encapsulated
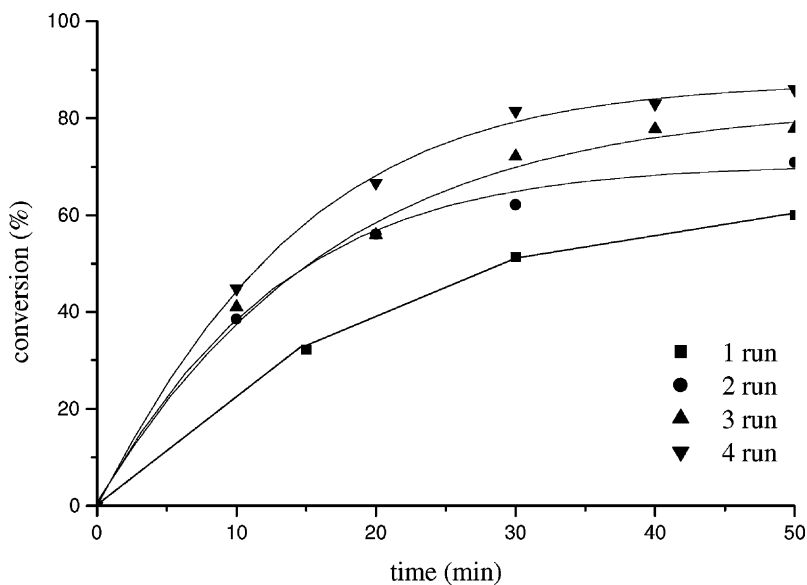

Fig. 8. Recycling experiments of catalyst MCM-Mn**1b**: oxidation of (2-ethylbutyl) phenyl sulfide.
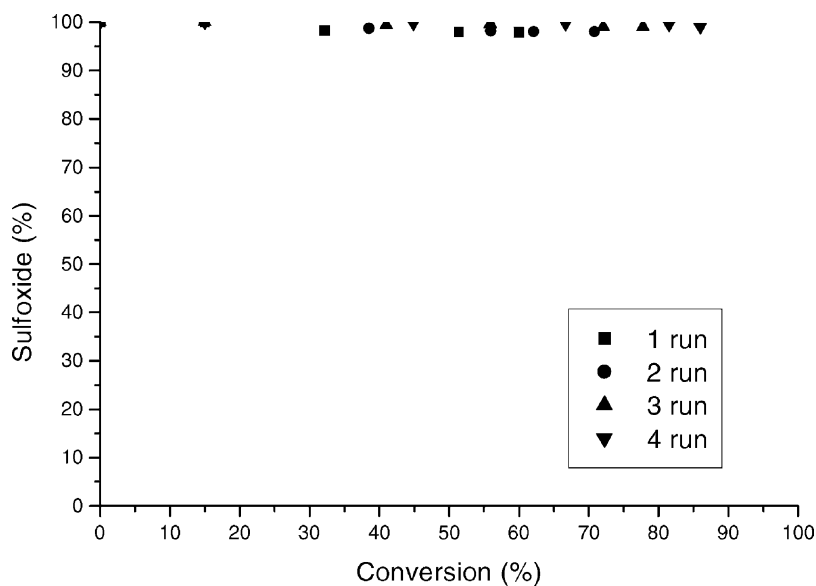
Fig. 9. Selectivity to (2-ethylbutyl) phenyl sulfoxide for the cycles of oxidation reactions carried out with MCM-Mn**1b**.

catalysts (Table 1, Fig. 3), compared to the homogeneous counterpart, could have been anticipated in view of the restrictions imposed on the diffusion substrate and products through the micropores of the solid, when the reaction is run at low temperatures, meanwhile, at room temperature, the turnover rates for the oxidation of methyl phenyl sulfide and (2-ethylbutyl) phenyl sulfide with the heterogeneous catalyst were found to be
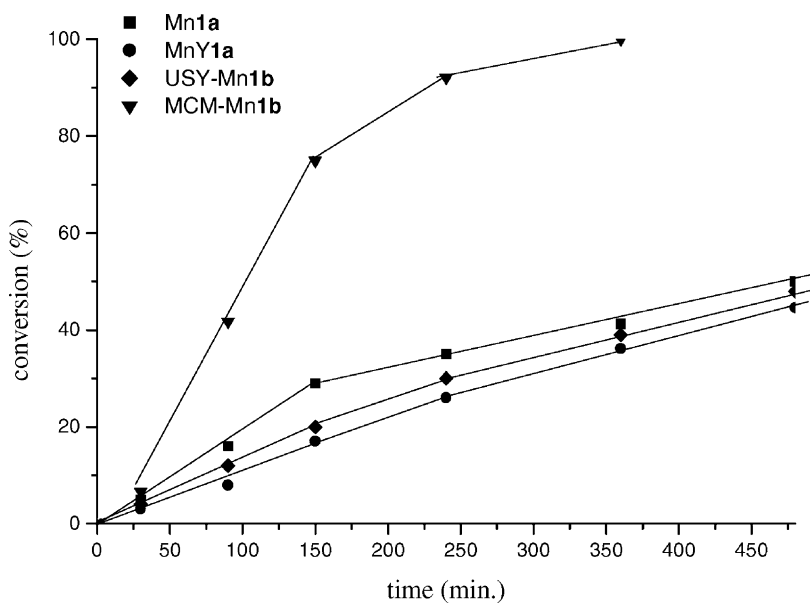

Fig. 10. Kinetic profile of oxidation of nerol with Mn-catalysts.

higher than those for the homogeneously catalysed reactions (Fig. 6), this fact is a consequence of the lower importance of diffusion at higher temperatures.

In all these experiments moderate enantiomeric excesses were obtained, as shown by GC analysis of the reaction mixture using a chiral column or ^{1}H-NMR of the purified sulfoxide. Since the highest enantiomeric excesses reported in the literature were observed using PhIO, sulfoxidation of methyl phenyl sulfide with this mild oxidant was also carried out (Table 2, Fig. 5). Although the activity of the catalysts decreases (conversion >80 was achieved after 24 h in all cases), in the presence of PhIO, in this case an increase of the enantioselectivity was observed. This increase is partly important when Mn**2a** and MCM-Mn**2b** were used as catalysts. When the reactions were carried out using H_2O_2 as oxidating agent the oxidation activity is lower and 10% of sulfoxide was obtained after 24 h.

For homogeneously catalysed reactions, the termination of catalytic cycle may occur because of two factors, due to the formation of Mn–O–Mn species, which has poor catalytic activity, or due to the oxidative degradation of metal complexes. This was confirmed by taking the IR spectra of the solid after catalytic reaction. The IR spectra of these solids are very different from that of the IR spectra of the parent compounds. To improve the stability of the metal complex under the reaction conditions we have heterogenised the complexes by preventing the catalytic species from dimerizing or aggregation, and to tune the selectivity of the reaction using the walls of the pores of the solid via steric effects.

The most important advantage of heterogeneous catalysis over its homogeneous counterpart are a high increasing of the complex stability in the reaction media and the possibility of reusing the catalyst after reaction by simple filtration (Fig. 8). The catalyst could be reused at least four times without neither loss of selectivity (Fig. 9) nor activity with catalyst loading as low as 1 mol%. While the oxidation of sulfide continued in presence of the catalyst, there was no further significant conversion when the catalyst was removed from the reaction system. This conclusion was independently confirmed by the absence of manganese in the filtrate (atomic absorption spectroscopy). On the other hand, all Mn and Cu catalyst, specially the heterogeneous one, with an excess of

oxidant and/or long times of reaction yields, as sole product, the corresponding sulfone with excellent yield.

4.2. Oxidation of nerol

The soluble and heterogenised Mn-complexes were tested for the epoxidation of (Z)-3,7-dimethyl-2,6-octadien-1-ol (nerol) used as model, with NaOCl as oxygen source at 0 °C in CH_2Cl_2 solutions. The results are summarised in Table 4.

Even though for test reactions we have only used 1% of molar ratio catalysts/substrate the conversion of allylic alcohol is generally high. The reactions showed a high chemoselectivity. Indeed, in most of the cases at 0 °C (conversion = 20%) epoxides were obtained as the main or sole products as detected by GC analysis. The results of the competitive epoxidation of nerol summarised in Table 4 indicate the preferential epoxidation of 2, 3 position. This is suggestive of the fact that the linear olefin is sterically more approachable to the active sites due to the coordination of OH to Mn center and prevent the 6, 7 position accessing the active sites at an effective rate. Chlorinated products, arising from chlorine addition to the C=C double bond were detected by GC–MS under the reaction conditions. Products arising from the nucleophilic aperture of the epoxide ring commonly observed for other non-enantioselective zeolite-catalysed epoxidations were absent [25]. The time-course plots of the epoxidation of nerol are shown in Fig. 10. The results obtained for heterogenised catalysts are generally comparable with the corresponding soluble manganese complexes which show a similar pattern indicating that both reactions take place through the same mechanism, without any significant change in the reaction pathway.

The lifetimes of the zeolite catalysts were examined by their repeated use in the epoxidation of nerol. The amount of metal ion was determined for each run. Approximately >95% of the metal was still retained on the zeolite anchored complex (90% for encapsulated) after five runs. The yield of epoxide decreased only slightly and notable change in selectivity has not been observed.

The high activity and selectivity and the significantly easier workout indicate that this type of catalysts is a truly heterogeneous counterpart of

homogeneous transition metal complex catalysts for epoxidation of allylic alcohols.

5. Conclusions

Manganese and copper complex cations, $[MnLCl]^+$, $[CuL]^+$, have been incorporated into molecular sieves. Heterogenisation of M(II)-complexes, with C_2-symmetry ligands, on USY-zeolite (containing supermicropores and a large quantity of silanol groups) and MCM-41 increases the activity of the homogeneous catalysts for different substrates. Mn(II)-complexes can be, also, immobilised in the intra-crystalline voids of Y zeolite. The resulting host/guest compounds are active catalysts for the oxidation of sulfides to sulfoxides and sulfones with very low catalyst/substrate ratio. The heterogenised complexes are significantly more stables than the corresponding homogeneous complexes over prolonged reaction times, and therefore better catalysts than homogeneous ones.

For all reactions tested, and for all heterogenised catalysts (encapsulated and anchored), a high selectivity in competitive reactions is observed for bulky substrates, which is correlated to molecular sieving effects (reactants size, selectivity effect), and a better regioselectivity is obtained (the 2 position favoured over the 6, 7 position in the oxidation of nerol). For encapsulated complexes these good selectivities are associated with lower activities (when operating at low temperature) due to diffusion limitations, not found at higher temperatures.

To summarise, zeolite-heterogenised complexes show interesting catalytic properties in oxidation reactions and these properties are related to the changes in the microenvironment of the ligand metal complex, caused by the support. The balance between the heterogeneous and homogeneous character can explain the success of our catalysts. These catalysts can be recovered and reused at least four times retaining most of their catalytic activity.

All the enantioselective enzymatic systems in nature have in common the incorporation of the active sites into a confined space defined by the tertiary protein structure. Our chiral heterogenised catalysts mimic this strategy: the rigid, inorganic framework of the zeolite determines the reaction cavity surrounding the active catalyst.

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