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Homogeneous and encapsulated within the cavities of zeolite Y chiral manganese and copper complexes with C_2-multidentate ligands as catalysts for the selective oxidation of sulphides to sulfoxides or sulfones

M.J. Alcón [a], A. Corma [b], M. Iglesias [a,*], F. Sánchez [c,1]

[a] *Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas (CSIC), Cantoblanco 28049 Madrid, Spain*
[b] *Instituto de Tecnología Química, UPV-CSIC, Avda de los Naranjos, 46022 Valencia, Spain*
[c] *Instituto de Química Orgánica CSIC, Consejo Superior de Investigaciones Científicas (CSIC), Juan de la Cierva 3, 28006 Madrid, Spain*

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Abstract

A series of manganese and copper complexes with tetradentate C_2-symmetry ligands, [Mn(C_2-ligand)Cl(H_2O)]PF_6 and [Cu(C_2-ligand)]ClO_4, have been synthesised and characterised as homogeneous and encapsulated into the supercages of a large pore sized USY zeolite. These Mn and Cu complexes are excellent catalysts for the selective oxidation of organic sulphides to sulfoxides or sulfones with high selectivity, and moderate to low enantioselectivity. The chelation of zeolite-exchanged Mn^{2+} by C_2–N-containing ligands gives rise to a whole class of heterogeneous liquid phase oxidation, which exhibits similar catalytic performances than the homogeneous ones. Moreover, those heterogenised catalysts can be recycled in successive runs, by a simple filtration, without a significant loss of activity and selectivity.

Keywords: Manganese; Encapsulated; Zeolite; Oxidation; Heterogenised

1. Introduction

The use of chiral catalysts has become a powerful methodology in modern synthetic organic chemistry [1–5]. As far as oxygen-transfer catalysis is concerned, the Sharpless–Katsuki epoxidation of allylic alcohols constituted an authentic breakthrough in this field [6–8]. More recently, Jacobsen and Zhang expanded the scope of the catalytic asymmetric epoxidation to some families of unfunctionalised alkenes with high stereocontrol by using chiral (salen) Mn complexes [9]. The recent results of Bonchio et al. [10] shows the state-of-the-art for sulfoxidation catalysts (based on Ti, Zr).

A further logical improvement of this homogeneous catalytic method would consist of the incorporation of the catalyst on to a support, making it possible to perform the reaction heterogeneously [11]. For manganese three approaches have been adopted: (i) supporting Mn epoxidation catalysts on polymers [12,13] or zeolites [14]; (ii) ion exchange of manganese complexes into the intra-crystalline space of zeolites,

* Corresponding author. Tel.: +34-91-5622900/ext. 258/34-91-3349032; fax: +34-91-3720623/34-91-5644853.
E-mail addresses: marta.iglesias@icmm.csic.es, felix-iqo@iqog.csic.es (M. Iglesias).
[1] Co-corresponding author.

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e.g. zeolite Y [15,16] or mesoporous materials [17]; and (iii) encapsulation of manganese complexes within zeolites by synthesis using "ship-in-a-bottle" methodology [18,19].

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.

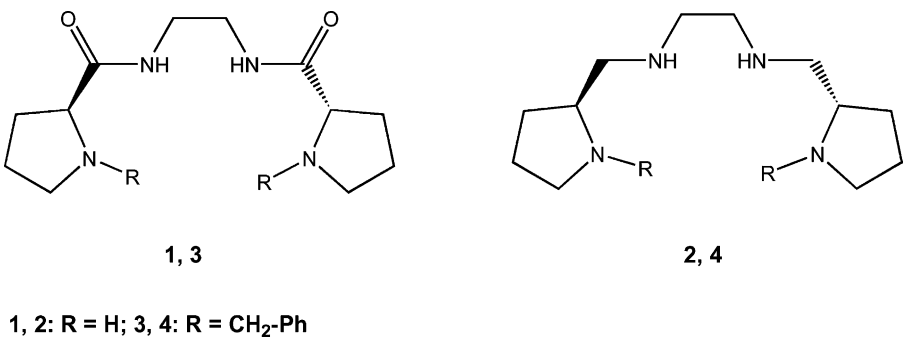
The use as chiral catalysts of Mn complexes embedded within zeolite opens a new methodology that allows a wide variety of reaction conditions, while diminishes the deactivating process owing to Mn complexes dimerisation. Furthermore, on top of the selectivity the overall process would benefit of the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

Although the heterogenisation strategy has been well established in oxidation processes [20–23] in the present contribution, we report our results on the synthesis and characterisation of a series of Mn(II) complexes with multidentate C_2-symmetry ligands (Fig. 1), [Mn(C_2-ligand)Cl(H_2O)]PF_6 and the heterogenisation of such complexes by 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 functionalised zeolite materials exhibited higher catalytic activity than the corresponding homogeneous catalyst and showed no significant loss of catalytic activity when recycled. A comparative study with analogous homogeneous copper complexes was also made.

2. Experimental

2.1. General

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. The zeolite samples were degassed at 100 °C and 10^{-2} Pa for 1 h prior to recording the spectra. ^1H, ^{13}C NMR spectra were taken on Varian XR300 and Bruker 200 spectrometers. ^1H NMR chemical shifts are given in ppm using tetramethylsilane as an internal standard. Optical rotation values were measured at the sodium-D line (589 nm) with a Perkin-Elmer 241MC polarimeter. Gas chromatography analysis was performed using a Hewlett-Packard 5890 II with a flame ionisation detector in a cross-linked methylsilicone column. MnY zeolite was prepared starting from NaY by ion exchange using a 5 mM aqueous solution of $Mn(CH_3COO)_2$ and 1-to-10 solid-to-liquid weight ratio. The resulting MnY zeolite containing 1.6Mn^{2+} ions per unit cell (which corresponds to an average of Mn^{2+} every five supercages) was filtered, washed with deionised water and air-dried at 373 K for 48 h. The inorganic support was dried at 415 K under 0.01 Torr before the heterogenisation process.



1, 3 **2, 4**

1, 2: R = H; 3, 4: R = CH_2-Ph

Fig. 1. C_2-symmetry ligands.

2.2. Synthesis of complexes

The ligands *N*,*N*′-bis[(*S*)-prolyl]ethylenediamine (**1**), *N*,*N*′-bis{[(*S*)-pyrrolidin-2-yl]methyl}ethylenediamine **(2)**, *N*,*N*′-bis[(*S*)-*N*-benzylprolyl]ethylenediamine (**3**), *N*,*N*′-bis{[(*S*)-*N*-benzylpyrrolidin-2-yl] methyl}ethylenediamine **(4)**, used in the present investigation have been prepared in our laboratory [24]. To a solution of ligand (1 mmol) in ethanol (30 cm^3) was added $MnCl_2{\cdot}4H_2O$ (198 mg, 1 mmol) and NH_4PF_6 (162 mg, 1 mmol) and the mixture was refluxed for 3 h. In the case of amide ligands, 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. For amine ligands, the solvent was evaporated until 5 ml and the addition of ethyl ether causes the precipitation of a brown solid which is filtered, washed and dried in vacuo.

2.2.1. {*Mn(N,N′-bis[(S)-prolyl]ethylenediamine)Cl*}PF_6

[Mn(**1**)Cl(H_2O)]$PF_6{\cdot}H_2O$ (**I**); white. Yield: 60%; mp = 186–194 °C; $[\alpha]_D^{25} = -95$ (1, EtOH); Λ_M (10^{-3} M, $\Omega^{-1}\,cm^2\,mol^{-1}$, CH_3CN) = 138–159. $C_{12}H_{26}ClF_6MnN_4O_4P$ (526): calc. C, 27.4; H, 5.0; N, 10.7; Mn, 10.4. Found: C, 27.5; H, 5.2; N, 10.6; Mn, 10.4%. IR (KBr, cm^{-1}): ν = 3406, 3252 (N–H); 1652, 1622 (C=O); 1550 (N–C=O); 836 (P–F). UV–VIS (10^{-3} M, DMF): λ nm ($\log\epsilon$) = 317.0 (2.3); 284.0 (2.3). MS (*m*/*z*): 398 ([Mn(**1**)]PF_6–3F–Cl); 345 ([Mn(**1**)Cl]$^+$); 255 ((**1**) + 1). TG analysis: 0.321 mg weight loss (6.81% of 4.71 mg complex; expected weight loss: 6.86%) at 123 °C.

2.2.2. {*Mn(N,N′-bis{[(S)-pyrrolidin-2-yl]methyl}ethylenediamine)Cl*}PF_6

[Mn(**2**)Cl(H_2O)]PF_6 (**II**); brown. Yield: 85%; mp = 122–125 °C; $[\alpha]_{546}$ = 10.8 (0.1, EtOH); Λ_M (10^{-3} M, $\Omega^{-1}\,cm^2\,mol^{-1}$, CH_3CN) = 158–179. $C_{12}H_{28}ClF_6MnN_4OP$ (480): calc. C, 30.0; H, 5.9; N, 11.7; Mn, 11.4. Found: C, 30.1; H, 6.0; N, 11.5; Mn, 11.2%. IR (KBr, cm^{-1}): ν = 3420, 3240 (N–H); 830 (P–F); δ = 1630 (N–H). UV–VIS (10^{-3} M, DMF): λ nm ($\log\epsilon$) = 340.0 (2.8); 324.5 (2.7); 285.5 (2.7). MS (*m*/*z*): 349 ([Mn(**2**)Cl]PF_6–6F + 1); 316 ([Mn(**2**)Cl]$^+$ − 1); 281 ([Mn(**2**)]$^+$); 227 ((**2**) + 1). TG analysis: 0.170 mg weight loss (3.70% of 4.60 mg complex; expected weight loss: 3.74%) at 120 °C.

2.2.3. {*Mn(N,N'-bis[(S)-N-benzylprolyl]ethylenediamine)Cl*}PF_6

[Mn(**3**)Cl(H_2O)]$PF_6{\cdot}2H_2O$ (**III**); white. Yield: 80%; mp = 128–132 °C (d); $[\alpha]_D^{25} = -32.0$ (0.5, EtOH); $[\alpha]_{546} = -36.0$ (0.5, EtOH); Λ_M (10^{-3} M, $\Omega^{-1}\,cm^2\,mol^{-1}$, CH_3CN) = 143–159. $C_{26}H_{40}ClF_6MnN_4O_5P$ (724): calc. C, 43.1; H, 5.6; N, 7.7; Mn, 7.6. Found: C, 43.3; H, 5.6; N, 7.3; Mn, 7.2%. IR (KBr, cm^{-1}): ν = 3398 (N–H); 1670 (C=O); 1554 (N–C=O); 839 (P–F). UV–VIS (10^{-3} M, DMF): λ nm ($\log\epsilon$) = 282.50 (2.7). MS (*m*/*z*): 556 ([Mn(**3**)Cl]PF_6–6F); 435 (**3**). TG analysis: 0.334 mg weight loss (7.36 % of 4.54 mg complex; expected weight loss: 7.46%) at 118 °C.

2.2.4. {*Mn(N,N'-bis{[(S)-N-benzylpyrrolidin-2-yl]methyl}ethylenediamine)Cl*}PF_6

[Mn(**4**)Cl(H_2O)]$PF_6{\cdot}3H_2O$ (**IV**); brown. Yield: 66 %; mp = 105–111 °C; $[\alpha]_D^{25} = -13.3$ (0.15, EtOH); Λ_M (10^{-3} M, $\Omega^{-1}\,cm^2\,mol^{-1}$, CH_3CN) = 166–177. $C_{26}H_{46}ClF_6MnN_4O_4P$ (714): calc. C, 43.7; H, 6.5; N, 7.8; Mn, 7.7. Found: C, 43.9; H, 6.8; N, 7.4; Mn, 7.2%. IR (KBr, cm^{-1}): ν = 3420 (N–H); 840 (P–F); δ = 1620 (NH). UV–VIS (10^{-3} M, DMF): λ nm ($\log\epsilon$) = 318.5 (2.3); 285.5 (2.4). MS (*m*/*z*): 495 ([Mn(**4**)Cl]$^+$ − 2); 407 (**4**). TG analysis: 0.437 mg weight loss (10.00% of 4.37 mg complex; expected weight loss: 10.08%) at 107 °C.

The copper complexes were synthesised as described in a previous paper [25].

2.3. Heterogenisation of manganese complexes: 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 CH_2Cl_2 solution containing the adequate ligand (1 mmol). The resulting suspension was magnetically stirred at reflux temperature for 12 h, filtered and washed exhaustively with CH_2Cl_2. Finally, the white or brown Mn-ligand zeolite sample was Soxhlet extracted with CH_2Cl_2 to reduce the presence of unreacted and surface species from the zeolite particles.

Residual uncomplexed Mn on zeolite could 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-ligand zeolite complexes were stirred with aqueous solutions of $NaNO_3$ (0.1 M) to re-exchange uncomplexed manganese ions. Finally, the solid was filtered and dried in vacuo. Elemental analysis indicated 1.82 (MnY1), 1.32 (MnY2), 1.36 (MnY3), 1.35 (MnY4) mass percent of Mn.

IR (KBr, cm^{-1}):

MnY1 $\nu = 3410, 3250$ (N–H); 1650, 1620 (C=O); 1234 (very strong, sup.); 1083 (very strong, sup.).

MnY2 $\nu = 3396, 3240$ (N–H); 1236 (very strong, sup.); 1080 (very strong, sup.); $\delta = 1630$ (N–H).

MnY3 $\nu = 3398, 3300$ (N–H); 1670 (C=O); 1233 (very strong, sup.); 1083 (very strong, sup.).

MnY4 $\nu = 3400, 3368$ (N–H); 1235 (very strong, sup.); 1080 (very strong, sup.); $\delta = 1620$ (N–H).

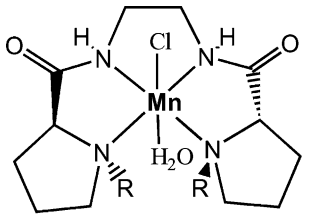
2.4. Catalytic activity: oxidation of sulphides catalysed by M(C_2-ligand) complexes

All oxidation reactions were carried out by the following procedure: the catalyst (0.01 mmol) was added to a dichloroethane solution of the substrate (sulphide, 1 mmol) and 4-methylmorpholine N-oxide monohydrate (0.1 mmol). The mixture was heated at desired temperature and an aqueous solution of the oxidant NaOCl (pH = 11.3, 1.9 mmol) was added. Chemical yields and the enantiomeric excesses of methylphenylsulphide were measured by gas chromatography 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) [26]. The ee for (2-ethylbutyl)phenylsulphide was determined by ^1H NMR using (-)MPPA ((*R*)-(-)-α-methoxyphenylacetic acid) [27] as chiral shifting agent.

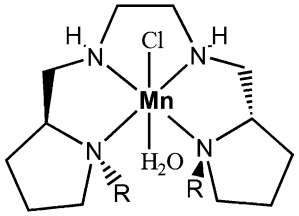
3. Results and discussion

3.1. Synthesis of complexes

The C_2-multidentate ligands were synthesised following our previously described procedure, which describes the advantages of easy accessibility to a wide family of N-donor ligands [24]. $MnCl_2{\cdot}4H_2O$ reacted with ligands **1**–**4** in presence of NH_4PF_6 to yield the cationic complexes, $[Mn(ligand)Cl(H_2O)]PF_6{\cdot}xH_2O$, (**I**–**IV**). Acetonitrile solutions of these complexes were highly conductive [28]; this implied that there was extensive dissociation of the chloride ligand upon dissolution of complexes and consequent formation of the respective cation $[Mn(ligand)(solvent)_2]^{2+}$. Unfortunately, we could not grow any single crystals suitable for X-ray crystallographic studies. The Mn complexes (**I**–**IV**) described herein all involve the ligands functioning as a neutral, tetradentate chelate through its amine, amide groups. The structures of complexes demonstrate the considerable flexibility in the conformations that multidentate



I: R = H
III: R = Bz



II: R =H
IV: R = Bz

Fig. 2. Structure of new complexes.

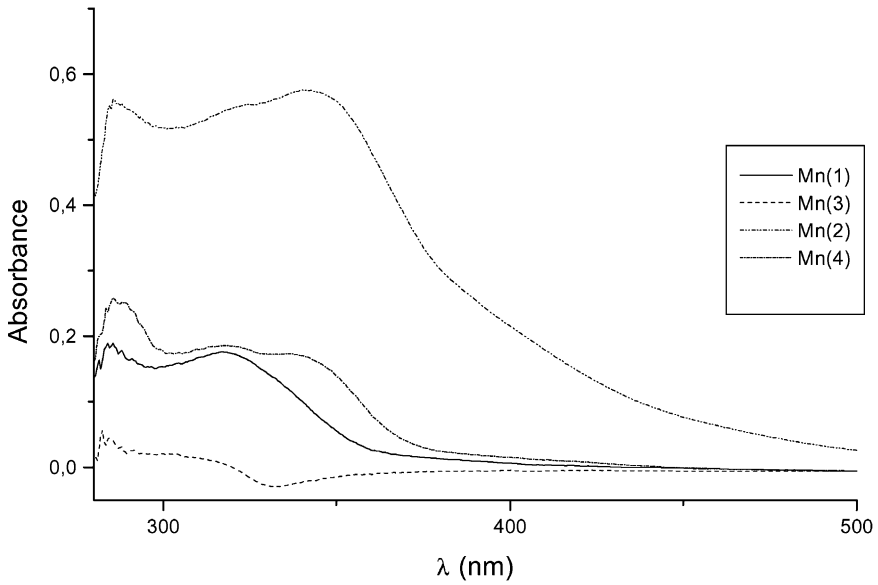


Fig. 3. Electronic spectra of [Mn(C_2-symmetry ligand)Cl(H_2O)]PF_6.

ligands can adopt (Fig. 2). The co-ordinating solvents have been verified by the appropriate losses in their thermogravimetric (TG) analyses. The new complexes are air-stable microcrystalline solids.

The IR spectra of the free ligands exhibit the characteristic bands of amides and amines. The amide I band appears at about 1650–1670 cm^{-1} and amide II at 1530–1550 cm^{-1}. The IR spectrum of complex **(I)** shows a ν(N–H) band at 3406 cm^{-1}, shifted due to Mn-coordinated NH (pyrrolidine ring) and a broad band at 3252 cm^{-1} shifted to lower frequencies that corresponds to ν(N–H) amide band. The amide bands appears splitted at 1652, 1622 cm^{-1}, close to the free ligand position and corresponds to the uncoordinated carbonyl function. The amide II band appears in the same position as the free ligand. The ν(P–F) frequency appears at 836 cm^{-1}. The IR spectrum of complex **III** shows ν(N–H) bands and a strong intensity absorption band at 1670 cm^{-1} attributable to the ν(C=O) vibration, appears in the same position that the free ligand that excludes co-ordination to the C=O. The IR spectra of amine–Mn complexes show ν(N–H) frequencies and bands due to ν(P–F) at 830 cm^{-1}. The compounds show a broad band at 3300–3500 cm^{-1} indicative of co-ordinated and lattice water.

The electronic spectra of all the complexes, in DMF, show intraligand transition bands at 320 and 280 nm, while the MLCT bands fall near 350 nm. The position of the MLCT band depends on functional group amide or amine (Fig. 3). As expected for Mn(II) complexes, d–d transition bands are not observed in dilute solution because of their being doubly forbidden.

The FAB, ESI-MS and APCI-MS mass spectra of complexes were recorded. All the complexes examined provided nice quality ionspray mass spectra and the molecular weight of the complex has been confirmed in all cases. The ionisation of these compounds occurs with loss of PF_6 ion, finding in all cases a cationic $[Mn(L)Cl]^+$ species. Also, these complexes tend to give a heterolitic breakage of the M–X bond. The Mn–Cl bond present in these complexes is indeed quite polarised and it breaks affording the complexes metal cation by loss of a chloride anion. In the mass spectra of the complex **I**, peak at $m/z = 345$ corresponds to the cationic ion $[Mn(\mathbf{1})Cl]^+$, $m/z = 398$ to loss of chlorine and fluorine anions in the parent compound, $m/z = 255$ to ligand. For the compound $[Mn(\mathbf{2})Cl]PF_6$, the peak at 349 corresponds to parent ion with loss of fluorine, $m/z = 316$ to $[Mn(\mathbf{2})Cl]^+ - 1$, $m/z = 281$ to $[Mn(\mathbf{2})]^+$, $m/z = 227$ to ligand. In

case of **III** peak at $m/z = 556$ corresponds to parent compound with loss of fluorine anions and peak at $m/z = 435$ to ligand. For complex **IV**, peak at $m/z = 495$ corresponds to $[Mn(\mathbf{4})Cl]^+$ cationic species and $m/z = 407$ to ligand.

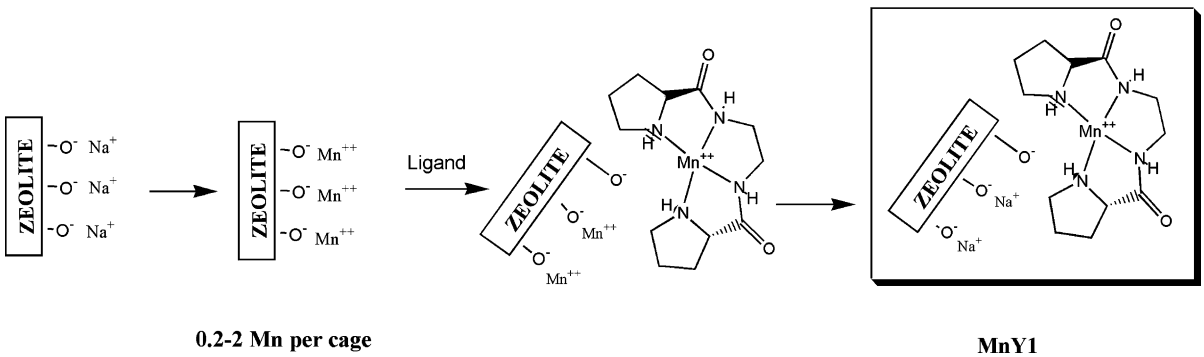
3.2. Heterogenisation of complexes

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 were exceptionally high. We have made the heterogenisation by encapsulating or encaging the catalyst in the voids of a porous inorganic solid (USY zeolite) (Scheme 1).

The objective, clearly, is to improve the stability of the metal complex under the reaction conditions by preventing the catalytic species from dimerising 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 **1**–**4** 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, 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 super cages 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 encapsulated complexes, as well as the crystallinity of the host zeolite. The IR bands of all encapsulated complexes are weak due to their low concentration in the zeolite. $Mn(C_2$-ligand) 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 complexes after incorporation into zeolite matrix.

The diffuse reflectance spectra of $Mn(C_2$-ligand) complexes are almost identical before and after encapsulation (Fig. 4), indicating that the complexes maintain their geometry even after encapsulation without significant distortion.



Scheme 1. Preparation of C_2-symmetry derived manganese complexes in the supercages of zeolite Y.

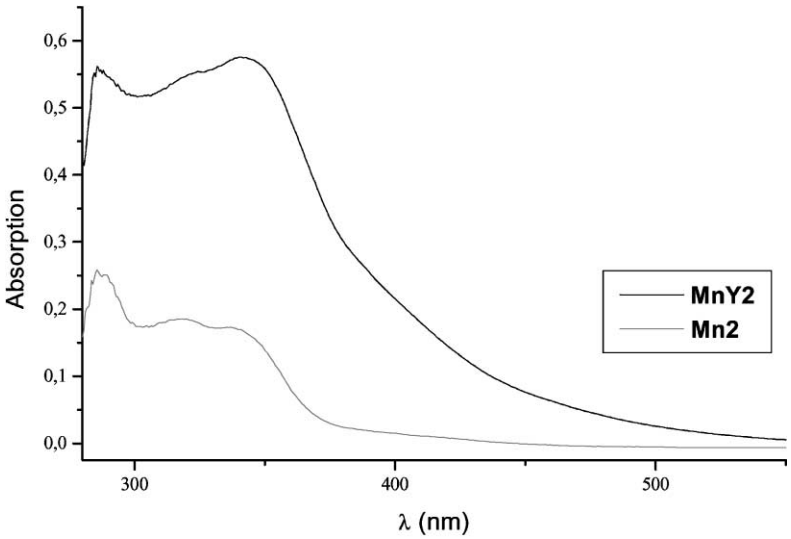


Fig. 4. UV–VIS diffuse reflectance spectra of Mn2 and MnY2.

4. Catalytic activity

In order to determine the performance of Mn and Cu complexes as catalysts, the oxidation of organic substrates, methylphenylsulphide, (2-ethylbutyl)phenylsulphide was tested. The activities, selectivity and enantiomeric excesses attained are collected in Tables 1–3, Figs. 5–12.

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 and consequently was employed as an oxidant in the present study. Also the pH of NaOCl

Table 1
Oxidation of alkylphenylsulphides catalysed by Mn(C_2-symmetry ligand) in homogeneous conditions

Substrate	Catalysts	T (°C)	Percent of conversion (h)	Selectivity of SO (%)	TOF[a]	ee (%)
Methylphenylsulphide	Mn1	Room temperature	77 (0.5)	40	458	18.6
		0	76 (2)	47	163	18.6
	Mn2	Room temperature	74 (1.5)	28	116	23.1
		0	89 (2.5)	69	197	26.5
	Mn3	Room temperature	68 (2)	38	218	14.6
		0	75 (2)	55	141	16.1
	Mn4	Room temperature	65 (1.5)	10	110	6.8
		0	75 (2)	40	166	15.7
(2-Ethylbutyl)phenylsulphide	Mn1	Room temperature	100 (2)	80	74	5
	Mn2	Room temperature	100 (2)	78	83	<5
	Mn3	Room temperature	78 (2)	75	58	<5
	Mn4	Room temperature	71 (2)	72	53	5

[a] Measured in mmol subs./mmol cat. min.

Table 2
Oxidation of alkylphenylsulphides catalysed by Cu(C_2-symmetry ligand) in homogeneous conditions

Substrate	Catalysts	T (°C)	Percent of conversion (h)	Selectivity of SO (%)	TOF[a]	ee (%)
Methylphenylsulphide	Cu1	0	86 (3)	51	103	18.5
	Cu2	0	100 (3)	48	120	30
	Cu3	0	92 (3)	29	126	30
	Cu4	0	68 (3)	22	43	9
(2-Ethylbutyl)phenylsulphide	Cu1	Room temperature	100 (7)	78	22	4

[a] Measured in mmol subs./mmol cat. min.

Table 3
Oxidation of alkylphenylsulphides catalysed by Mn(C_2-symmetry ligand) complexes encapsulated within Y zeolite

Substrate	Catalysts	T (°C)	Percent of conversion (h)	Selectivity of SO (%)	TOF[a]	ee (%)
Methylphenylsulphide	MnY1	0	76 (3)	33	73	18.8
	MnY2	0	60 (3)	30	40	4.3
	MnY3	0	73 (3)	23	30	10.8
	MnY4	0	80 (3)	33	32	7.6
(2-Ethylbutyl)phenylsulphide	MnY1	Room temperature	95 (1.5)	95	213	8
	MnY2	Room temperature	100 (2)	91	132	14
	MnY3	Room temperature	100 (3.5)	87	61	12
	MnY4	Room temperature	100 (2.5)	87	93	21

[a] Measured in mmol subs./mmol cat. min.

solution was varied to determine that pH = 11.3 is the optimum for oxidation reactions. The promoter is used to stabilise the Mn(V)=O complex formed in the oxidation cycle. Finally, low temperature (0 °C) was chosen when a small molecule was oxidised; when a more bulky sulphide was oxidised no reaction was observed and the reaction temperature has to rise to room temperature to increase the reaction rate.

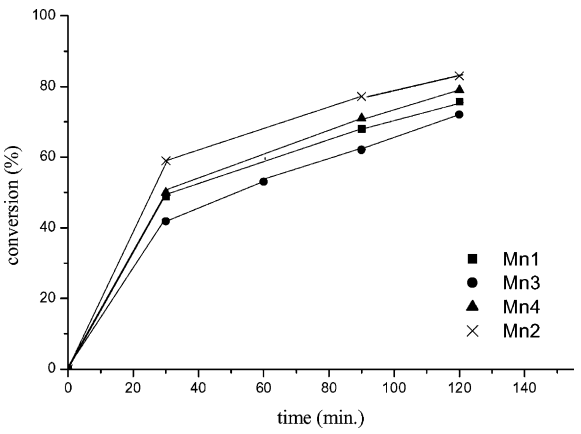


Fig. 5. Kinetic profile of oxidation of methylphenylsulphide with Mn-catalysts (T = 273 K).

The oxidations were usually carried out in the presence of catalytic amounts of the catalyst (1% based on experimental metal content) and 4-methylmorpholine N-oxide monohydrate (0.1 mmol) by using NaOCl as sacrificial oxidant in CH_2Cl_2 at 0 °C for methylphenylsulphide or 25 °C for (2-ethylbutyl)phenylsulphide. Higher reaction temperatures lead to a dramatic decrease in the selectivity to sulfoxide as well as a significant loss of the asymmetric induction. 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.

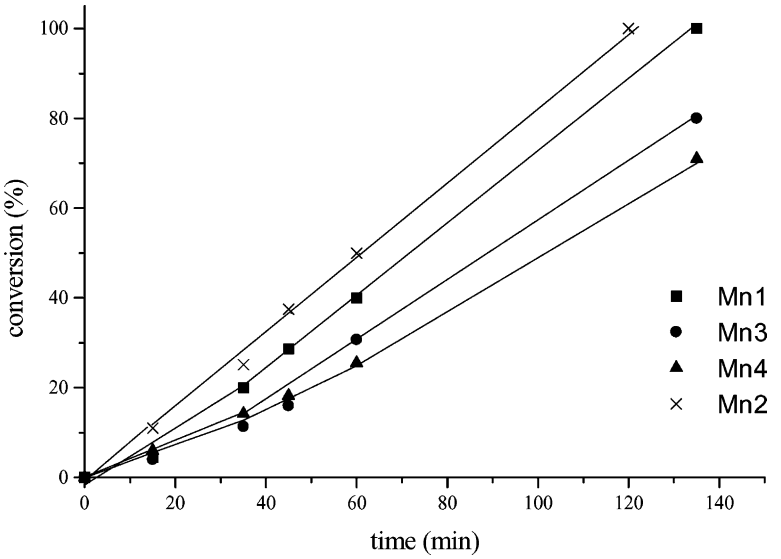


Fig. 6. Kinetic profile of oxidation of (2-ethylbutyl)phenylsulphide with Mn-catalysts (room temperature).

The reactions showed a high chemoselectivity for larger (2-ethylbutyl)phenylsulphide (Table 1, Fig. 10). Indeed, in most of the cases sulfoxides were obtained as the main or sole products as detected by GC, TLC and ^{1}H NMR analysis. Furthermore, products of the oxidation of the (2-ethylbutyl)phenylsulphide were not detected at 0 °C. The lower selectivity found for methylphenylsulphide corresponds with the much higher extent of the reaction with this substrate. As can be concluded from Table 1, methylphenylsulphide and (2-ethylbutyl)phenylsulphide 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 have quite the same reactivity.

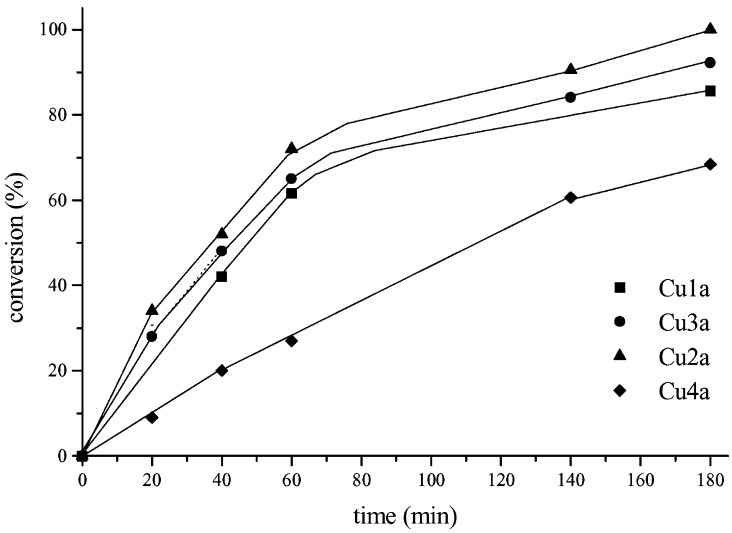


Fig. 7. Kinetic profile of oxidation of methylphenylsulphide with Cu(C_2-ligand) catalysts ($T = 273$ K).

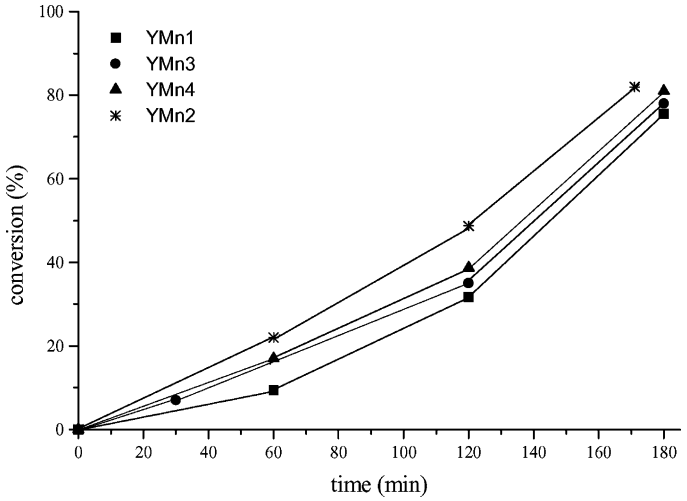


Fig. 8. Kinetic profile of oxidation of methylphenylsulphide with MnY(ligand) catalysts ($T = 273$ K).

As far as the catalyst is concerned, it can be seen that for the oxidation of alkylphenylsulphides (Tables 1 and 2) the presence of an amide group does not seem to have any major influence on the activity of the corresponding catalyst (Figs. 5 and 6) and similar selectivity was found with the former catalysts (Fig. 10). The amide compounds are slightly more effective catalysts than the amine-ones; these observations are in agreement with the fact that ligands bearing electron withdrawing groups should in principle be better catalyst, since a higher resistance to oxidative destruction and an activation of the catalyst must be achieved.

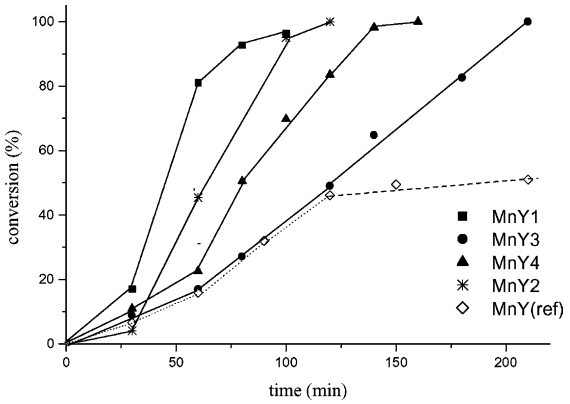


Fig. 9. Kinetic profile (2-ethylbutyl)phenylsulphide MnY(ligand) (room temperature).

The copper complexes show less activity (Fig. 7) and similar selectivity (Fig. 11) that manganese ones. This may be due to the fact that the formation of Cu-oxo species (catalytically active intermediate) is kinetically less favoured in this case.

The lower reaction rates obtained for the oxidation of methylphenylsulphide with the encapsulated catalysts (Table 3, Fig. 8), 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 methylphenylsulphide and (2-ethylbutyl)phenylsulphide with the heterogeneous catalyst were found to be higher than those for the homogeneously catalysed reactions (Fig. 9), this fact is a consequence of the lower importance of diffusion at higher temperatures.

Although the enantiomeric excess obtained using homogeneous and MnY complexes follow the same pattern, we noticed somewhat lower values (MeSPh) for the zeolite-bound catalysts. This can be interpreted as a combination of two unfavourable factors: (i) the occurrence of a non-catalysed, unselective oxidation routes in the liquid phase and/or; (ii) the existence of residual amounts of uncomplexed Mn^{2+} acting as catalytic sites.

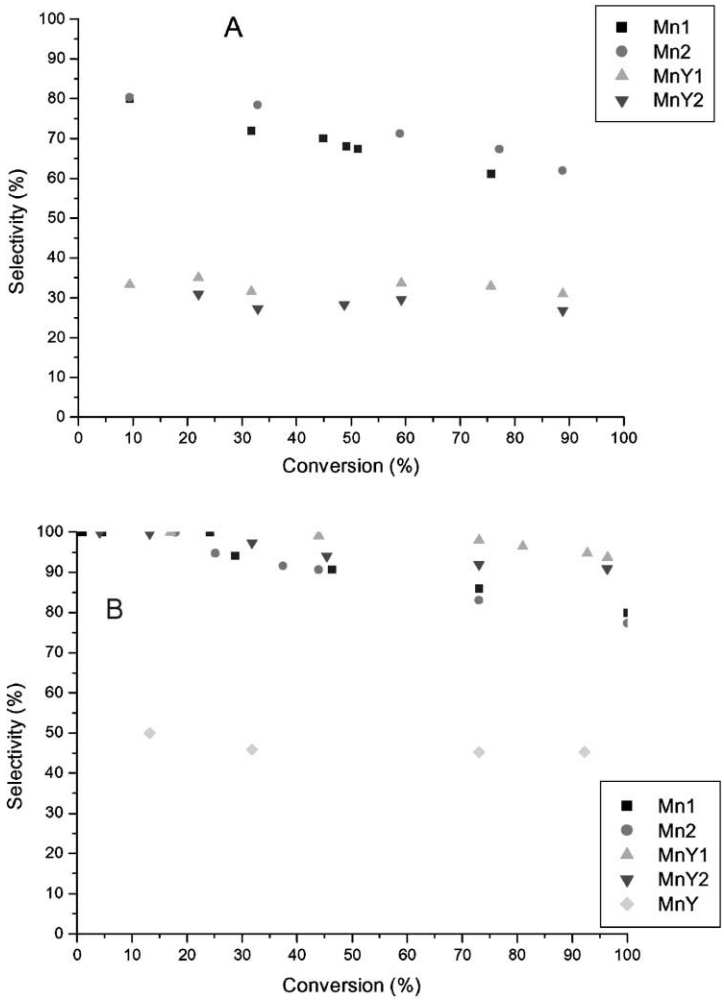


Fig. 10. Selectivity to methylphenylsulfoxide (A) and (2-ethylbutyl)phenylsulfoxide (B) for the oxidation reactions carried out with Mn-catalysts (homogeneous and encapsulated).

The above point raises the question of how to assess that the reaction is taking place inside the zeolite micropores. The simplest straightforward way to address this point is to determine the inactivity of the encapsulated complexes by using reagent of larger dimensions than the pore windows of zeolite host. It has been found [20–23] that a cyclic oligomeric precursor of PhIO gives similar results to those obtained using NaOCl. Therefore, this bulky reagent would be size excluded from the 7.4 Å faujasite pore windows. To further establish the lack of Mn leaching, we performed chemical analysis of the liquid phase after the reaction. Nor Mn ions neither catalytic activity could be detected.

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 much different from that of the IR spectra of the parent compounds. To improve the stability of the metal complex under the reaction conditions we

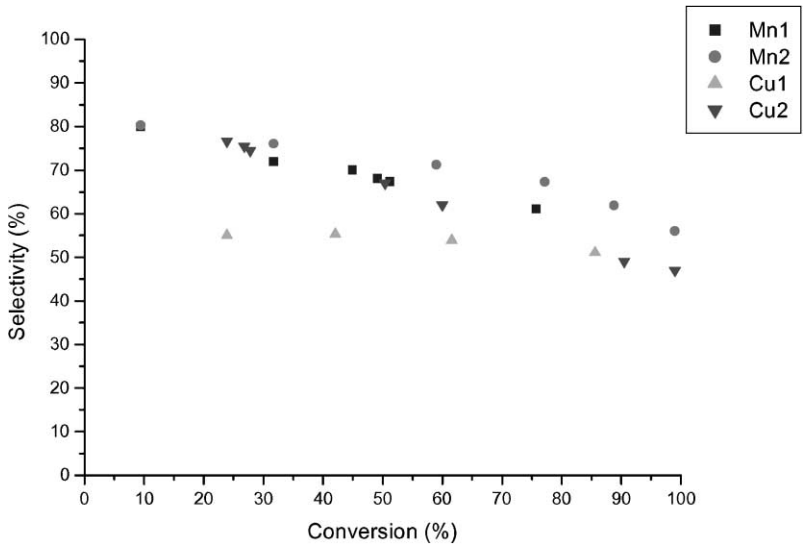


Fig. 11. Selectivity to methylphenylsulfoxide for the oxidation reactions carried out with Mn and Cu catalysts (homogeneous).

have heterogenised the complexes by preventing the catalytic species from dimerising 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 (Table 4). The catalyst could be reused at least four times without neither loss of selectivity (Fig. 12) nor activity with catalyst loading as low as 1 mol%. While the oxidation of sulphide 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

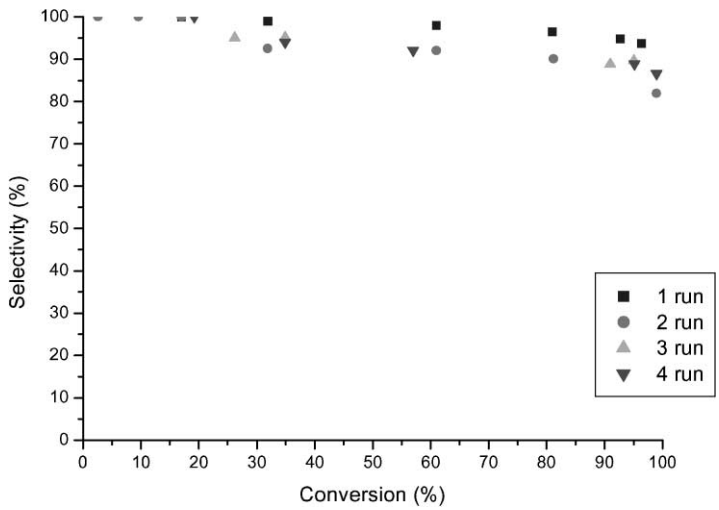


Fig. 12. Selectivity to (2-ethylbutyl)phenylsulfoxide for the cycles of oxidation reactions carried out with encapsulated MnY1-catalysts.

Table 4
Recycling of catalyst MnY1 for the oxidation of de(2-ethylbutyl) phenylsulphide

Run	Conversion (%)/*t* (h)	Selectivity (%)	TOF[a]	ee (%)
1	95/3.5	95	113	8
2	100/5	90	72	10
3	95/5	90	45	6
4	100/4	89	74	9

[a] Measured in mmol subs./mmol cat. min.

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.

5. Conclusions

Multidentate C_2-symmetry ligands and their manganese complexes have been encapsulated in the supercages of zeolite Y. The resulting catalysts have been characterised by various spectroscopic (IR, UV–VIS), thermal analysis, etc.

The manganese and copper complexes with C_2-symmetry ligands are selective catalysts for the oxidation of sulphides to sulfoxides and sulfones with very low catalyst:substrate ratio (0.01). Mn complexes can be immobilised by encapsulation in the intra-crystalline voids of USY zeolite, the resulting host/guest compounds which are also active catalysts for the selective oxidation of sulphides, moreover the heterogenised complexes are significantly more stable than their corresponding homogeneous complexes over prolonged reaction times, and therefore better catalysts than homogeneous ones.

For all reactions tested, 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. For encapsulated complexes these good selectivity are associated with lower activities (when operating at low temperature) due to diffusion limitations (Fig. 9), 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 greater stability is attributed to the suppression of dimeric and other polymeric oxo complexes of Mn due to geometric constraints on their formation on encapsulation in zeolites. 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.

Acknowledgements

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