

# Mesoporous MCM41-heterogenised (salen)Mn and Cu complexes as effective catalysts for oxidation of sulfides to sulfoxides

## Isolation of a stable supported Mn(V)=O complex, responsible of the catalytic activity

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### Abstract

Chiral salen manganese and copper complexes immobilised on mesoporous silica supports (silica, MCM-41) have been investigated as catalysts in the sulfide to sulfoxide oxidation; the supported catalysts are highly suited to reactions leading to high yields and high sulfoxide/sulfone selectivity while moderate asymmetric induction (up to 30%) was observed. The presence of stable manganese [Mn(V)=O] complexes into support channels have been established, being responsible for catalytic activity. The recovery and reusability of heterogenised Mn- and Cu-catalysts have been studied.

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### 1. Introduction

The selective oxidation of sulfides to sulfoxides has been a challenge for many years, partly due to the importance of sulfoxides as intermediates in organic synthesis. [1] Homogeneous catalysis often provides the best results in achieving high levels of enantioselectivity whereas heterogeneous catalysis offers the advantages of simplified product purification and the potential for catalyst recycling [2]. Clearly, heterogeneous catalysis which can provide high enantioselectivity would be an important development with potential applications in industrial and high-throughput organic chemistry [3].

In recent years, reactions catalyzed by chiral-salen based transition metal complexes have become a matter of interest [4]. In many cases, metal-salen complexes have been

immobilized on different materials, such as polymers [5] or inorganic solids such as silica [6] and zeolites [7]. Their interest is related with the fact that they perform highly selective processes in a multi-phase system, in where the catalysts can be easily recovered.

The immediate goals of our studies were (1) to evaluate the heterogenising method (2) the effect of supports on the sulfides oxidation and (3) to determine the extent to which heterogenised catalysts can be increased the stability of complexes in reaction media, and can be recycled for repeated use. The results are described herein.

### 2. Experimental

#### 2.1. Materials

All preparations of metal complexes were carried out under dinitrogen by conventional Schlenk-tube tech-

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niques. Solvents were carefully degassed before use. The silylating agent  $\text{OCN}(\text{CH}_2)_3\text{Si}(\text{OEt})_3$  was obtained from ABCR. C, H and N analysis were carried out by the analytical department of the Institute of Materials Science (C.S.I.C.) with a Perkin–Elmer 240C apparatus. Metal contents were analysed by atomic absorption using a Perkin–Elmer Analyst 300 atomic absorption spectrometer and plasma ICP Perkin–Elmer 40. IR spectra were recorded on a Bruker IFS 66v/S spectrophotometer (range  $4000\text{--}200\text{ cm}^{-1}$ );  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$  spectra were taken on Varian XR300 and Bruker 200 spectrometers. Chemical shifts being referred to tetramethylsilane (internal standard). Optical rotation values were measured at the sodium-D line (589 nm) with a Perkin–Elmer 241 MC polarimeter. Gas chromatography analysis was performed using a Hewlett–Packard 5890 II with a flame ionisation detector with a chiral capillary column (mixture of methyl silicone (OV-1701) and heptakis-[2,3-dipentyl-6-(*t*-butyldimethylsilyl)]- $\beta$ -cyclodextrine as stationary phase) [8]. The ee for (2-ethylbutyl) phenyl sulfide was determined by  $^1\text{H-NMR}$  using (–)-MPPA ((*R*)-(–)- $\alpha$ -methoxyphenylacetic acid) as chiral agent [9]. The inorganic supports for anchoring were silica gel, and purely siliceous MCM-41 [10].

## 2.2. Preparation of salen manganese and copper complexes

Catalysts were prepared as we previously described (Scheme 1 and 2) [11]. The (*S,S*)-*N,N'*-(3-*tert*-butyl-5-methylsalicylidene)-1,2-diaminocyclohexane (**5**) was obtained as by-product in the synthesis of the heterogenised

ligand. The corresponding manganese or copper compounds were synthesised as reported in the literature for similar complexes [12]. Typically, manganese (II) and copper (II) complexes were prepared by adding ethanolic solutions of  $\text{Mn}(\text{OAc})_2$  or  $\text{Cu}(\text{OAc})_2$  (0.5 mmol/15 ml) to a vigorously stirred slurries of the corresponding anchored salen ligands **4a**-(Sil), **4b**-(Sil), **4a**-(MCM-41), **4b**-(MCM-41) (over 0.5 mmol per gram) or **5** (233 mg, 0.5 mmol) in  $\text{CH}_2\text{Cl}_2$  (15 ml) at room temperature. The resulting mixture was refluxed for 4 hours and then concentrated under reduced pressure. The residue was Soxhlet extracted with ethanol-ether and dried in vacuum to afford the heterogenised complexes in almost quantitative yields.

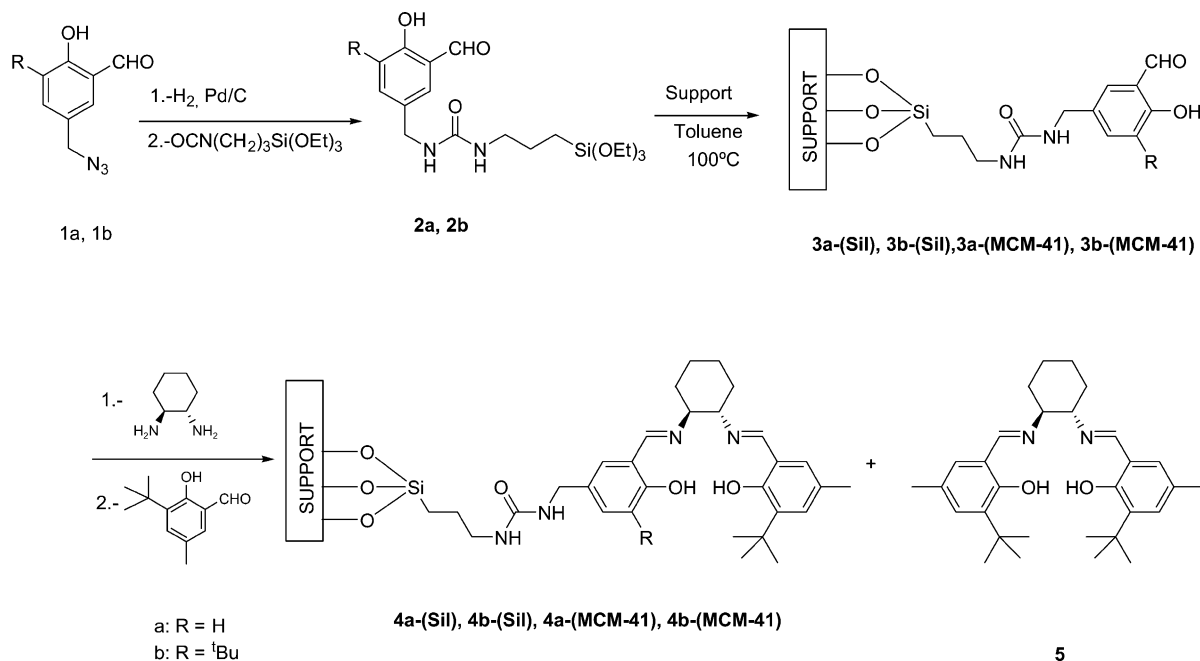
**4aMn**-(Sil): analysis found: C 8.89, H 1.46, N 1.84, Mn 2.03% gives 0.37 mmol/g; IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 1626$  (C=O), 1555 (C=N), 583 (Mn–O, br); IR (PET,  $\text{cm}^{-1}$ ):  $\nu = 466$ . UV–vis ( $\lambda$ , nm): 583, 467, 390.

**4bMn**-(Sil): analysis found: C 12.69, H 2.01, N 2.09, Mn 3.30% gives 0.60 mmol/g; IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 1628$  (C=O), 1550 (C=N), 566, 534 (Mn–O); IR (PET,  $\text{cm}^{-1}$ ):  $\nu = 468$ . UV–vis ( $\lambda$ , nm): 602, 472, 395.

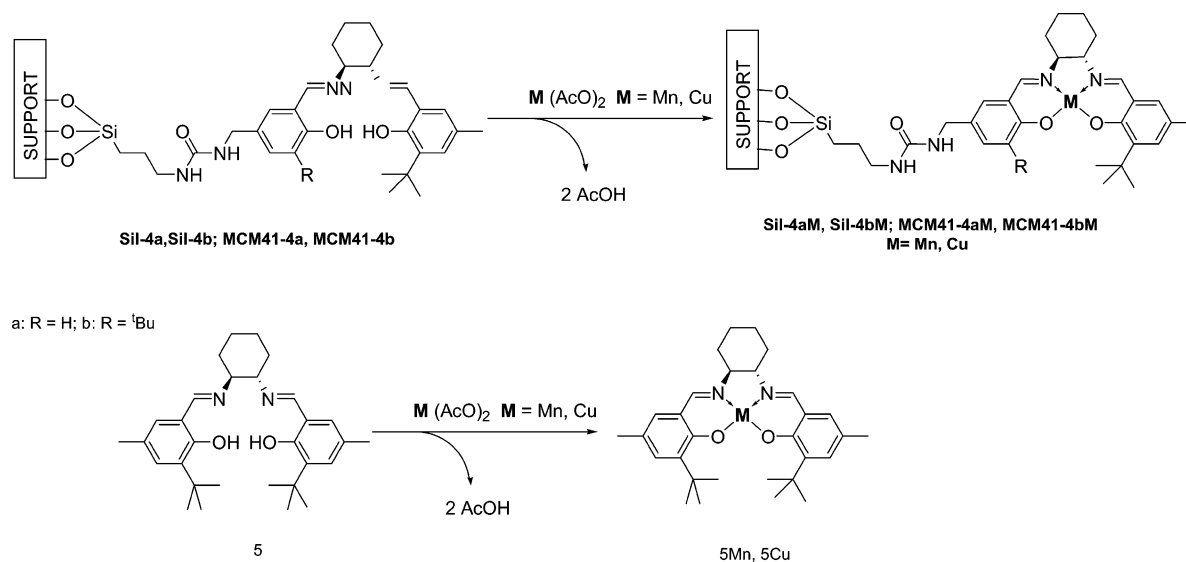
**4aMn**-(MCM-41): analysis found: C 8.93, H 2.55, N 1.91, Mn 2.36% gives 0.43 mmol/g; IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 1628$  (C=O), 1550 (C=N), 562 (Mn–O, br); IR (PET,  $\text{cm}^{-1}$ ):  $\nu = 466$ . UV–vis ( $\lambda$ , nm): 590, 415, 360.

**4bMn**-(MCM-41): analysis found: C 11.36, H 2.17, N 1.69, Mn 2.58% gives 0.47 mmol/g; IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 1628$  (C=O), 1564 (C=N), 564, 535 (Mn–O); IR (PET,  $\text{cm}^{-1}$ ):  $\nu = 466$ . UV–vis ( $\lambda$ , nm): 594, 467, 391.

**4aCu**-(Sil): analysis found: C 13.76, H 2.05, N 2.67, Cu 2.18% gives 0.34 mmol/g; IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 1623$  (C=O),



Scheme 1. Synthesis of ligands.



Scheme 2. Synthesis of complexes.

1556 (C=N), 552 (Cu–O, br); IR (PET,  $\text{cm}^{-1}$ ):  $\nu = 470$ . UV–vis ( $\lambda$ , nm): 565, 390, 365.

4bCu–(Sil): analysis found: C 16.41, H 2.71, N 2.60, Cu 1.99% gives 0.31 mmol/g; IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 1628$  (C=O), 1550 (C=N), 552 (Cu–O, br); IR (PET,  $\text{cm}^{-1}$ ):  $\nu = 470$ . UV–vis ( $\lambda$ , nm): 575, 405.

4aCu–(MCM-41): analysis found: C 15.19, H 2.73, N 2.46, Cu 1.98% gives 0.31 mmol/g; IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 1636$  (C=O), 1557 (C=N), 583, 555 (Cu–O); IR (PET,  $\text{cm}^{-1}$ ):  $\nu = 469$ . UV–vis ( $\lambda$ , nm): 565, 380.

4bCu–(MCM-41): analysis found: C 17.56, H 2.64, N 2.53, Cu 1.27% gives 0.20 mmol/g; IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 1628$  (C=O), 1564 (C=N), 550, 542 (Cu–O); IR (PET,  $\text{cm}^{-1}$ ):  $\nu = 469$ . UV–vis ( $\lambda$ , nm): 570, 380.

### 2.3. General procedure for oxidation reactions

#### 2.3.1. Preparation of heterogenised oxo-metal complexes

A mixture of heterogenised pre-catalyst (0.025 mmol), and the oxidant (0.03 mmol) in 1,2-dichloroethane was stirred for 24 h at 70 °C. The colour changes from black brown to light brown. The oxo-complex was isolated by filtration. The solid was exhaustively washed with a mixture of  $\text{CH}_2\text{Cl}_2$ -diethylether for removing any traces of oxidant and dried in vacuum.

4aMn(O)–(Sil): IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 1636$  (C=O), 1550 (C=N), 590 (Mn–O, br); IR (PET,  $\text{cm}^{-1}$ ):  $\nu = 466$ , 148. UV–vis ( $\lambda$ , nm): 464, 382, 270.

4bMn(O)–(Sil): IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 1636$  (C=O), 1555 (C=N), 541 (Mn–O); IR (PET,  $\text{cm}^{-1}$ ):  $\nu = 468$ , 148; UV–vis ( $\lambda$ , nm): 470, 390, 283.

4aMn(O)–(MCM-41): IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 1642$  (C=O), 1550 (C=N), 550 (Mn–O, br); IR (PET,  $\text{cm}^{-1}$ ):  $\nu = 466$ , 148. UV–vis ( $\lambda$ , nm): 410, 357, 272.

4bMn(O)–(MCM-41): IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 1642$  (C=O), 1568 (C=N), 550 (Mn–O); IR (PET,  $\text{cm}^{-1}$ ):  $\nu = 468$ , 147. UV–vis ( $\lambda$ , nm): 463, 385, 275.

4aCu(O)–(Sil): IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 1642$  (C=O), 1557 (C=N), 541 (Cu–O, br); IR (PET,  $\text{cm}^{-1}$ ):  $\nu = 466$ , 148. UV–vis ( $\lambda$ , nm): 572, 384, 360, 270.

4bCu(O)–(Sil): IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 1640$  (C=O), 1557 (C=N), 550 (Cu–O, br); IR (PET,  $\text{cm}^{-1}$ ):  $\nu = 466$ , 148. UV–vis ( $\lambda$ , nm): 584, 3955, 275.

4aCu(O)–(MCM-41): IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 1642$  (C=O), 1557 (C=N), 557 (Cu–O, br); IR (PET,  $\text{cm}^{-1}$ ):  $\nu = 466$ , 146. UV–vis ( $\lambda$ , nm): 582, 370, 270.

4bCu(O)–(MCM-41): IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 1636$  (C=O), 1564 (C=N), 557 (Cu–O, br); IR (PET,  $\text{cm}^{-1}$ ):  $\nu = 466$ , 148. UV–vis ( $\lambda$ , nm): 590, 370, 272.

#### 2.3.2. Oxidation reactions

**2.3.2.1. Supported catalysts.** The flask was charged with: (i) a suspension of the heterogenised oxo-catalyst (0.01 mmol) in  $\text{CH}_2\text{Cl}_2$  (3 ml); (ii) a solution of the substrate (1 mmol) in  $\text{CH}_2\text{Cl}_2$ ; (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), *t*-BuOOH (2.5 mmol),  $\text{H}_2\text{O}_2$  (30%, 3 mmol) or solid IOPH (2 mmol)] was added and the reaction mixture was stirred.

**2.3.2.2. Soluble catalysts.** In a typical oxidation reaction: a dichloroethane solution of the catalyst (0.01 mmol) was stirred with 1 mmol of the oxidant for 3 h at 60 °C. The mixture was allowed to desired temperature and the substrate (sulfide, 1 mmol), 4-methylmorpholine N-oxide monohydrate (0.1 mmol) and the oxidant were added. Chemical yield was measured by gas chromatography.

### 3. Results and discussion

#### 3.1. Preparation of heterogenised catalysts

The solids employed in the present study as supports of the (salen)Mn and Cu complexes were amorphous silica (used as reference support) with high surface area and all-silica MCM-41. These solids were selected to compare topologies. Thus, while silica is a non-porous material that has exclusively external surface in where the salen complex will be attached, in the case of MCM-41 the complex would be presumably located within the mesoporous channels (35–40 Å of diameter).

Anchoring of the (salen)complexes were made as depicted in Scheme 1 and 2. In this methodology, the (salen)complex is anchored to the solid by the phenolic ring through an urea-propyl chain. This strategy has a considerable advantage from other described in the literature [13] from the point of view of economy of synthetic steps. After preparation of the catalyst, the solids were characterised by thermo-gravimetric and elemental analysis, FTIR and diffuse reflectance UV–vis spectroscopy. The analytic data of the catalysts prepared as well as other relevant characteristics of the anchored salen complexes are indicated in experimental section.

The coordination sphere of manganese or copper ion is not involved in the anchoring of the complex to the support and, therefore, the activity of these supported complexes is expected to be similar to that of the same complex in solution. Giving that metal salen complexes exhibit characteristic metal-to-ligand transition bands in their optical spectra, anchoring of these complexes on the solid surface can be followed by DR UV–vis spectroscopy of the resulting catalysts. The diffuse reflectance UV–visible spectra shown in Fig. 1 are typical of chiral salen Mn (III) complexes. The chiral salen ligands of Mn (III) form showed the broad bands at near 250, 290, 390 and 500 nm on the UV-spectra. But the Mn salen complex showed no absorption peak at about 300 nm. The broad bands are probably due to charge-transfer transitions in

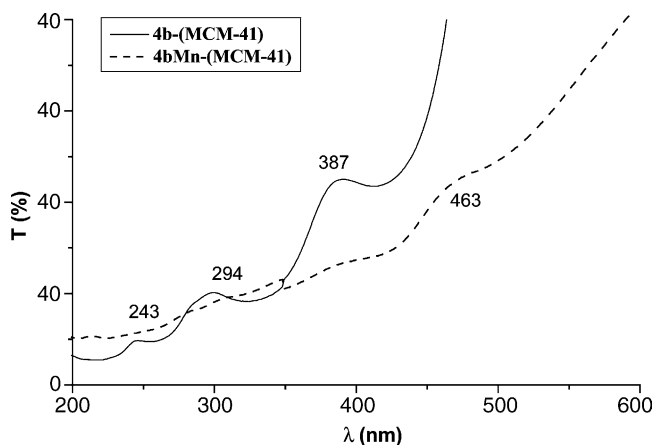


Fig. 1. The diffuse reflectance UV–vis spectra of the heterogenised chiral salen ligand (—) and the heterogenised chiral (salen)Mn complex (---).

the Mn ions and charge-transfer transitions between the metal and ligand, respectively [14]. The characterisation of the samples was also carried out using FTIR spectroscopy after immobilizing the salen complexes onto the MCM-41 and silica. In the IR spectra, all the salen complexes as well as MCM-41 and silica loaded chiral salen ligand exhibit the characteristic imine stretching vibration. For uncomplexed salen ligands this band appears at 1564 (heterogenised) and 1590 (homogeneous)  $\text{cm}^{-1}$  and upon addition of the metal ions the values change to lower frequency (1550 and 1540  $\text{cm}^{-1}$ ). This shift agrees with reported data [15]. The spectra also show bands due to M–O vibration at 560 (Mn–O), 550  $\text{cm}^{-1}$  (Cu–O).

##### 3.1.1. Supported M-oxo-(salen)complexes

Addition of *t*-BuOOH (2 equivalent) to a reaction suspension containing dark brown supported-(salen)complexes at 60 °C caused after 24 h generation of a stable new light brown species with a new band at ~270 nm (Fig. 2). DR-IR also shows a new band at ~146  $\text{cm}^{-1}$ . The formation of oxo-complexes was also observed in the reactions of salen-complex with other oxidants such NaOCl, and iodobenzene under identical reaction conditions. On the basis of the UV–vis and IR spectral features of this intermediate we suggest that this complex, generated in the reactions of *t*-BuOOH and other single oxygen atom donors, is an oxomanganese (V) salen complex. The oxidised compounds are very stable, even after six months, and maintained their catalytic activity. This stability is due to site-isolation of complexes, which precludes their dimerisation/oligomerisation to less reactive  $\mu$ -oxo species.

##### 3.1.2. Homogeneous oxo-complexes

Homogeneous oxo-complexes were obtained in the same way that supported ones but they were used without isolation from the reaction medium due to the oxidative degradation of metal complexes. This was confirmed by taking the IR spectra of the solid after the addition of the oxidant. The IR spectra of these solids are very much different from that of the IR spectra of the parent compounds, indicating that the complex undergoes oxidative degradation during the oxidation reaction.

#### 3.2. Catalytic behaviour of soluble and heterogenised complexes

##### 3.2.1. 3.2.1A comparative study

The selective oxidation of sulfides to sulfoxides has been a challenge for many years, partly due to the importance of sulfoxides as intermediates and versatile chiral building blocks for organic synthesis [16] and much effort has been directed toward asymmetric oxidation of sulfides. In recent years selective oxidation of sulfides to sulfoxides has been carried out with a large number of heterogeneous and supported reagents [17]. We have tested the soluble and heterogenised Mn- and Cu-(salen)complexes and the respective oxo-derivatives in the oxidation of methyl phenyl sulfide and

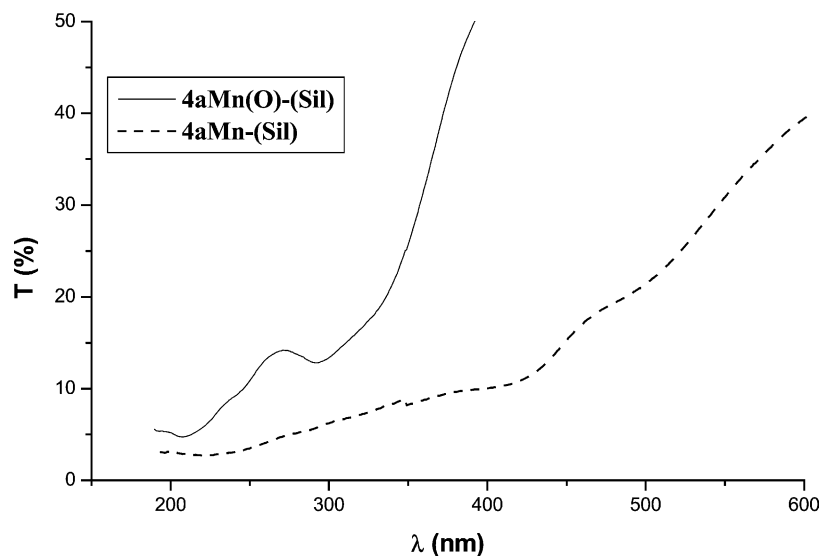


Fig. 2. The electronic spectra of complex 4aMn(Sil) (---) and 4aMn(O)-(Sil) (-).

(2-ethylbutyl) phenyl sulfide. When we have used the original salen-complexes for oxidation process, they are not active and high temperature is necessary for the reaction. If activated salen-oxo-complex was used the reaction takes place at low temperature.

The active discussion of the mechanistic principles of the oxidation reaction [18] led us to evaluate the intermediates of this reaction. The oxygen donor oxidizes the original  $Mn^{3+}$  to  $Mn^{5+}$ , and an intermediate oxo complex is produced. The reactivity of this intermediate was examined in sulfide oxidation reactions, by generating the intermediate and using them in reactivity studies. When a sulfide substrate was added to a reaction mixture containing the intermediate oxo complex generated in the reaction of salen-complex with a stoichiometric amount of oxidant, the intermediate reverted to the starting brown manganese (III) salen complex, demonstrating that the intermediate is capable of oxidizing the sulfide to give the sulfoxide product. Furthermore, when more oxidant was added to a reaction suspension containing (salen)Mn and substrate, the oxo complex was formed upon addition of oxidant and then decayed back to the starting  $Mn^{III}$ -complex. Finally, the UV-vis spectrum of the recovered supported catalyst did not change respect to starting intermediate oxo-complex (Fig. 3).

The catalytic activities of the (salen)complexes immobilised on silica and MCM-41 and the homogeneous complexes of same structure in solution were examined for the oxidation of organic sulfides (methyl phenyl sulfide and (2-ethylbutyl) phenyl sulfide) and the results of reactions are summarized in Tables 1 and 2. For effects of oxidants, first, hydrogen peroxide ( $H_2O_2$ ) was examined as oxidant in acetonitrile and conversion <10% was detected at ambient temperature in spite of excess amount of oxidant used whilst a mild oxidant NaOCl acts as a better oxidant yielding higher 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).

The main product of oxidation of alkyl phenyl sulfide with homogeneous and supported salen complexes, at room temperature, is the sulfoxide. Product of oxidation of sulfoxide was mainly formed at conversions higher than 80%. No significant changes in product distribution are observed when the whole amount of oxidant is added in one single stage or gradually added during the course of the reaction.

To determine any matrix effects on the rate of the reaction, the kinetics and selectivity curves of the oxidation of

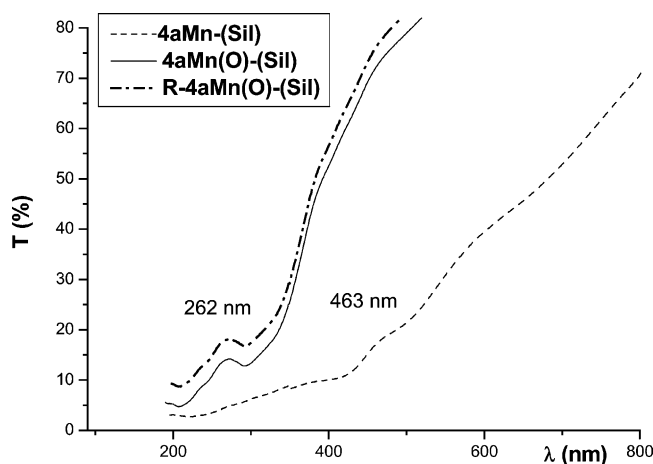


Fig. 3. The electronic spectra of complex 4aMn(Sil) (---) and 4aMn(O)-(Sil) (-) and recovered 4aMn(O)-(Sil) (-.-).

Table 1  
Results obtained in the oxidation of methyl phenyl sulfide promoted by different activated supported salen catalysts

Catalysts	Oxidant	Conversion (5 h) <sup>a</sup>	Selectivity (SO) <sup>b</sup>	TOF <sup>c</sup>	ee (%) <sup>d</sup>
5Mn	<i>t</i> -BuOOH	74	70	630	1
	IOPh	76	83	620	27
4aMn-(Sil)	<i>t</i> -BuOOH	26	100	160	3
	NaOCl	45	65	1050	9
	NaOCl + NMO	53	96	1220	12
4bMn-(Sil)	<i>t</i> -BuOOH	39	91	210	8
	NaOCl	54	92	820	3
	NaOCl + NMO	68	97	1080	11
	IOPh	44	92	180	20
4aMn-(MCM-41)	<i>t</i> -BuOOH	36	100	300	< 5
	NaOCl	61	89	850	< 5
	NaOCl + NMO	68	98	1000	< 5
4bMn-(MCM-41)	<i>t</i> -BuOOH	19	100	110	5
	NaOCl	28	75	730	< 5
	NaOCl + NMO	36	100	980	8
	IOPh	30	94	150	26
5Cu	<i>t</i> -BuOOH	94	100	520	< 5
4aCu-(Sil)	<i>t</i> -BuOOH	55	88	200	< 5
4bCu-(Sil)	<i>t</i> -BuOOH	78	93	400	< 5
4aCu-(MCM-41)	<i>t</i> -BuOOH	70	87	300	< 5
4bCu-(MCM-41)	<i>t</i> -BuOOH	87	96	490	< 5

<sup>a</sup> Total conversion was achieved at 24 h reaction time.

<sup>b</sup> Amount of sulfoxide/amount of sulfide consumed.

<sup>c</sup> TOF: mmol substr./mmol cat. h.

<sup>d</sup> ee determined by GC-MS and <sup>1</sup>H-NMR.

methyl phenyl sulfide catalysed by homogeneous, and heterogenised 4aMn-(Sil) and 4aMn-(MCM-41) were compared (Figs. 4 and 5). When the salen-immobilised MCM-41 was used as a catalyst, the pore structure of the mesoporous support had an effect on the catalytic activity for the sulfoxidation. The conversions of sulfide to sulfoxide were found to decrease over the MCM-41 support. Table 1 show that an equivalent quantity of homogeneous complex in solution was more active for sulfide oxidation than the immobilised coun-

Table 2  
Results obtained in the oxidation of (2-ethylbutyl) phenyl sulfide promoted by different activated supported salen catalysts (oxidant = *t*-BuOOH)

Cat.	Conversion (5h) <sup>a</sup>	Selectivity <sup>b</sup> (SO)	TOF <sup>c</sup>	ee (%) <sup>d</sup>
5Mn	53	74	640	6
4aMn-(Sil)	42	90	280	10
4bMn-(Sil)	50	92	220	16
4aMn-(MCM-41)	40	93	270	10
4bMn-(MCM-41)	41	92	250	7
5Cu	78	97	620	4
4aCu-(Sil)	30	87	305	2
4bCu-(Sil)	28	93	290	3
4aCu-(MCM-41)	42	89	320	11
4bCu-(MCM-41)	70	90	540	6

<sup>a</sup> Total conversion was achieved at 24 h reaction time.

<sup>b</sup> Amount of sulfoxide/amount of sulfide consumed.

<sup>c</sup> TOF: mmol substr./mmol catalyst (h).

<sup>d</sup> ee determined by GC-MS and <sup>1</sup>H-NMR.

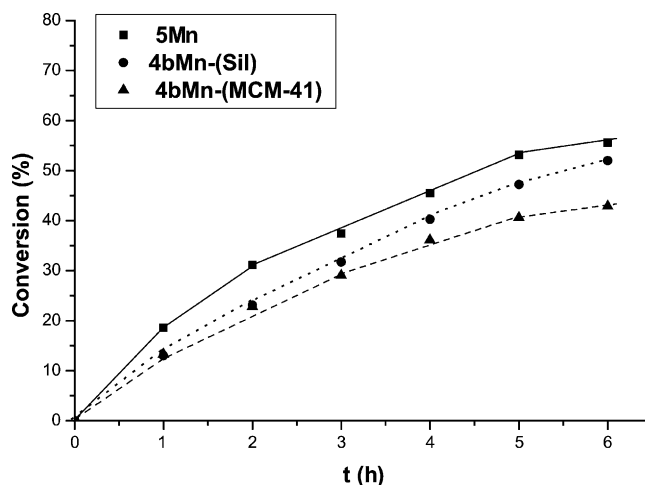


Fig. 4. Kinetic profile for the oxidation of methyl phenyl sulfide with homogeneous and heterogenised Mn-catalysts.

terpart. The lower activity of the anchored complex may be due to diffusion problems associated with the support.

In all these experiments moderate enantiomeric excesses were obtained, as shown by gas chromatography analysis of the reaction mixture using a chiral column or <sup>1</sup>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 1, Fig. 6). Although the activity of the catalysts decreases, in the presence of PhIO, in this case an increase of the enantioselectivity was observed. It is interesting to note that, in general, the heterogenised catalysts gave equivalent enantiomeric excess as the soluble catalysts.

### 3.3. Catalyst recycles

The most important advantage of heterogeneous catalysis over its homogeneous counterpart is a high increasing of the complex stability in the reaction media and the possibility

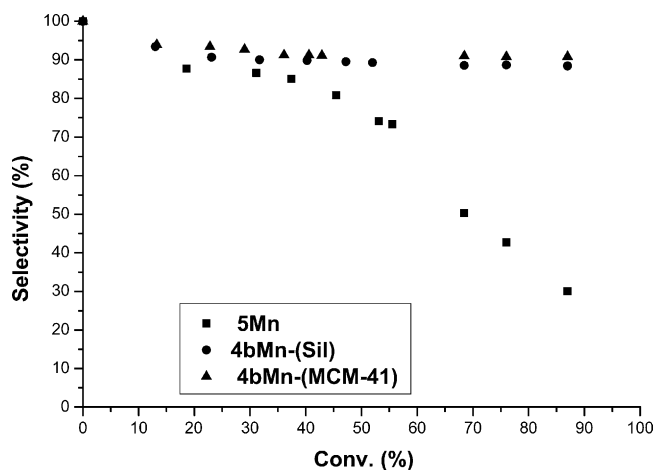


Fig. 5. Selectivity for the methyl phenyl sulfide oxidation with homogeneous and supported catalysts.



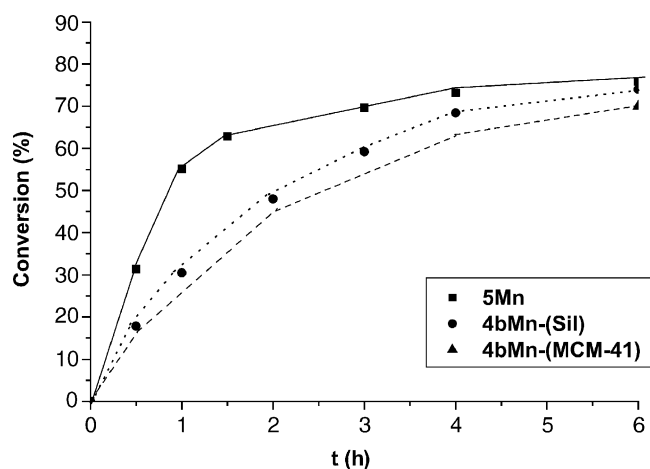


Fig. 6. Kinetic profile for the catalysed oxidation of methyl phenyl sulfide with IOPh as oxidant.

Table 3

Recovery of the catalyst in the oxidation of methyl phenyl sulfide with *t*-BuOOH promoted by 4bMn-(MCM-41)

Run	Conversion (%) (6 h) <sup>a</sup>	TOF <sup>b</sup>
1	65	920
2	74	1050
3	68	960
4	65	992
5	64	1000

<sup>a</sup> Total conversion was achieved at 24 h reaction time.

<sup>b</sup> TOF: mmol substr./mmol catalyst (h).

of reusing the catalyst after reaction by simple filtration. We have selected the catalyst 4bMn-(MCM-41) using methyl phenyl sulfide as a model substrate for the recycling study. After using M(salen)complexes immobilised on silica and MCM-41 as catalysts, the resultant solution exhibited no colour and any presence of metal was not detected in the solution (as we confirmed by atomic absorption spectroscopy). 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 means that M(salen)complexes immobilised on inorganic support are stable during the reaction and exist in the system without any extraction. The catalytic activity and selectivity of immobilised M(salen)complexes have not changed after four times of reusing (Table 3). The catalyst could be reused after washing with CH<sub>2</sub>Cl<sub>2</sub> and drying under vacuum at 70 °C.

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. Conclusions

(Salen)manganese and copper complexes have been incorporated into inorganic supports, and we have demonstrated the high stability and reactivity of its oxomanganese

(V) species. Heterogenisation of metal-complexes, on silica (containing a large quantity of silanol groups) and mesoporous MCM-41 increases the activity of the homogeneous catalysts for different substrates. The resulting host/guest compounds are active catalysts for the oxidation of sulfides to sulfoxide and sulfone being the heterogenised complexes, significantly more stable 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 a high selectivity in competitive reactions is observed for bulky substrates, which is correlated to molecular sieving effects (reactants size, selectivity effect). 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 determines the reaction cavity surrounding the active catalyst.

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