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Chiral manganese(III) salen catalysts immobilized on MCM-41 and delaminated zeolites ITQ-2 and ITQ-6 through new axial coordinating linkers

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Abstract

We report that the catalytic behavior and enantioselectivity of three different chiral Mn(III) salen complexes anchored to traditional supports such as MCM-41 (38-Å pore diameter) and delaminated zeolitic materials ITQ-2 and ITQ-6 strongly depend on whether the complexes are attached to the surfaces through the chiral equatorial tetradentate salen ligand or via the apical ligand. As for the case of unsupported complexes, this experimental observation has been accounted for strong variations in the conformational preference of the catalyst intermediate toward the approaching olefin, as well as to unfavorable structural changes in the complex. In addition, control of the hydrophobicity of the surface allows for optimization of selectivity in obtaining chiral epoxides.

Keywords: Manganese; Salen; Asymmetric epoxidation; Delaminated zeolites

1. Introduction

Chiral salen based complexes reported by Jacobsen and Katsuki have emerged as efficient catalysts for enantioselective epoxidation of simple olefins [1,2].

Soon after these works, intense efforts were made to prepare the heterogeneous version of these chiral metal complexes in an attempt to make possible their recovery and recycling. Thus, chiral manganese salen complexes have been encapsulated within the supercages of faujasites Y and EMT, showing moderate to good stereoselectivity albeit with strong reduction of activity due to diffusion control of reactants within the pores of the zeolites [3]. Alternatively, they have been immobilized on a variety of organic and inorganic matrices (some of them with pore diameters ranging in the mesoporous range) with moderate to excellent results [4–10].

In this respect, we report here three new Mn(III) salen catalysts immobilized through the equatorial and apical positions of the complexes on the MCM-41 and delaminated materials ITQ-2 and ITQ-6 [11–13]. In all cases, the preparation of the supported catalysts implies the design of the appropriate vinyl monomer bearing the Mn(III) salen functionality and subsequent radical anti-Markonikov addition of a mercaptoalkoxysilane group that will act as linker or spacing group between the catalyst and the support.

We show that these heterogeneous chiral manganese complexes do effectively catalyze the epoxidation reaction of prochiral alkenes no matter the position of anchoring, although only those complexes fixed to the support through the apical coordinating ligand afford high levels of enantioselectivity. This striking change in chirality has been attributed to the replacement of bulky substituents around the active Mn^{3+} ion and the failure to create a stereogenic environment, as well as to unfavorable catalyst distortions involving the planar salen ligand when the complex is anchored through the robust salen-type ligand [1a,14,15].

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On the other hand, we show that this methodology is reasonably effective for improving the retention of the monomeric manganese salen complexes to the supports and allow recycling of the catalyst with only moderate loss of activity and stereoselectivity.

2. Experimental

2.1. *Synthesis of [(R,R)-N,N′-bis(3-tert-butyl-5-vinylsalycilidene)-1,2-cyclohexanediamine] manganese(III) chloride (**1**)*

The chiral catalyst **1** was obtained through the synthetic sequence designed by Salvadori et al. and given in Scheme 1 as follows: 3-*tert*-butyl-2-hydroxybenzaldehyde was converted to 3-*tert*-butyl-5-(chloromethyl)-2-hydroxybenzaldehyde by a classic chloromethylacion method [5a,16]. This chloromethylated compound was treated with triphenylphosphine in refluxing benzene to give a phosphonium salt. Subsequent Wittig reaction of this phosphonium salt with formalin under strongly basic conditions yielded a vinyl-substituted salicylaldehyde derivative. The final chiral salen ligand was easily formed on refluxing this vinyl salicylaldehyde derivative in ethanol with $(1R,2R)$-1,2-diaminocyclohexane. Ulterior treatment of the chiral salen ligand with $Mn(OAc)_2$ afforded the manganese complex **1**.

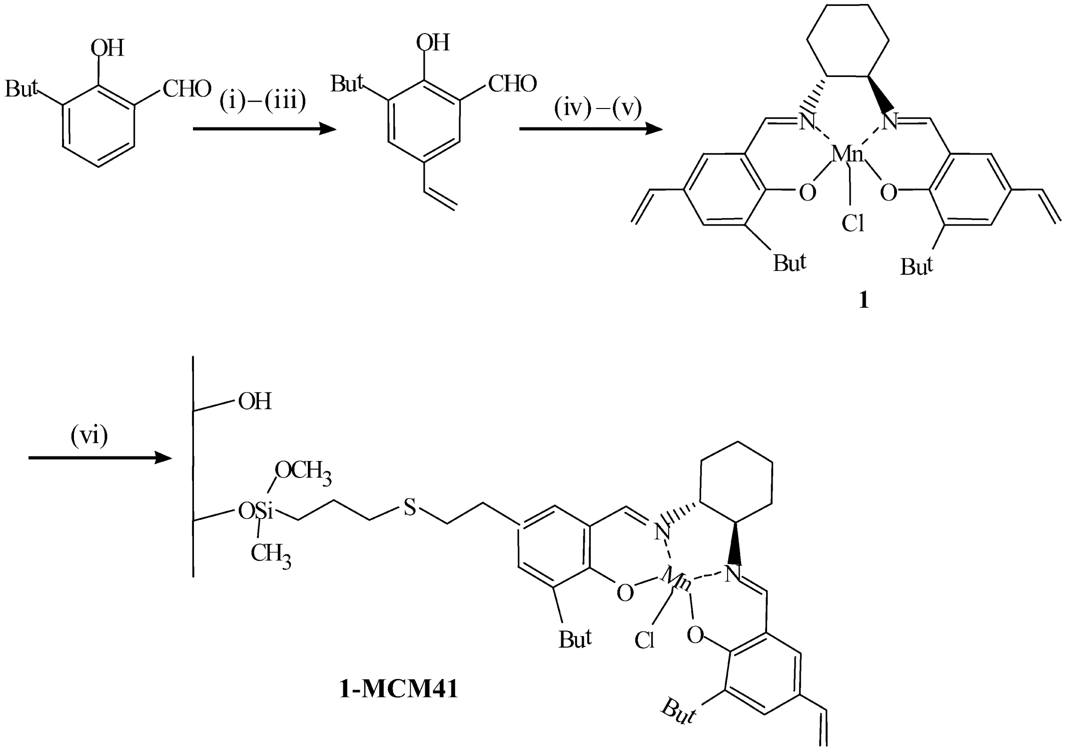
Characterization data for complex **1**: IR(KBr): 3450, 2950, 2904, 2863, 1630, 1600, 1540, 1452, 1395 cm^{-1}; UV–vis (CH_2Cl_2): 225, 275, 340, 412, 500 nm.

2.2. *Synthesis of [(R,R)-N,N′-bis-(3,5-di-tert-butylsalycilidene)-1,2-cyclohexanediamine] manganese(III) 6-heptenecarboxylate (**2**)*

A 50-ml round-bottom flask fitted with a dropping funnel was charged with 0.172 g (0.830 mmol) of $AgClO_4$ and 15 ml of dry CH_3CN. The dropping funnel was charged with a solution of 0.500 g (0.789 mmol) of Mn(salen)Cl complex in 25 ml of CH_3CN. The solution was added dropwise to the $AgClO_4$ solution in the flask and a precipitate formed almost immediately. The suspension was stirred at room temperature for 48 h and then filtered through Celite.

The filtrate was concentrated to a volume of 10 ml and 0.816 g (5.44 mmol) of sodium 6-heptenecarboxylate was added. The solution was stirred for 24 h, diluted with CH_3CN, and washed with H_2O. The organic phase was dried with Na_2SO_4, filtered, and concentrated to give 0.442 g of **2** as a brown powder ($R = 77\%$).

Characterization data for complex **2**: IR(KBr): 3452, 2950, 1610, 1545, 1106 cm^{-1}; UV–vis (CH_2Cl_2): 285, 300, 412, 510 nm; MS(FAB): m/z: 726 $[M]^+$, 599 M–$(CH_2{=}CH{-}(CH_2)_4{-}COO^-)]^+$, 584, 543.



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1-MCM41

Scheme 1. Schematic representation of the synthetic procedure followed for the immobilization of pure complex **1** on MCM41: (i) HCl, $(CH_2O)_n$; (ii) PPh_3; (iii) HCHO, NaOH; (iv) $(1R,2R)$-$(-)$-$C_6H_{10}(NH_2)_2$, EtOH, reflux; (v) $Mn(OAc)_2$, NaCl, EtOH, reflux; (vi) MCM41, Cl_3CH, AIBN, N_2, reflux.

2.3. Synthesis of [(R,R)-N,N′-bis(3,5-di-tert-butylsalycilidene)-1,2-cyclohexanediamine] manganese(III) 10-undecenoxide (3)

A 50-ml round-bottom flask fitted with a dropping funnel was charged with 0.172 g (0.830 mmol) of $AgClO_4$ and 15 ml of dry CH_3CN. The dropping funnel was charged with a solution of 0.500 g (0.789 mmol) of Mn(salen)Cl complex in 25 ml of CH_3CN. The solution was added dropwise to the $AgClO_4$ solution in the flask and a precipitate formed almost immediately. The suspension was stirred at room temperature for 48 h and then filtered through Celite.

The filtrate was concentrated to a volume of 10 ml, and 1.04 g (5.44 mmol) of sodium 10-undecenoxide were added. The solution was stirred for 24 h, diluted with CH_3CN, and washed with H_2O. The organic phase was dried with Na_2SO_4, filtered, and concentrated to give 0.48 g of **3** as a brown powder ($R = 77\%$).

Characterization data for complex **3**: IR(KBr): 3463, 2956, 1633, 1544, 1313, 1258, 1091 cm^{-1}; UV–vis (CH_2Cl_2): 212, 305, 420, 500 nm; MS(FAB): m/z: 754 $[M]^+$, 599 $[M–(CH_2{=}CH–(CH_2)_8–CH_2–O^-)]^+$, 584, 543.

2.4. Synthesis of MCM-41 and delaminated materials ITQ-2 and ITQ-6

Pure silica mesoporous MCM-41 (810 m^2/g) and pure silica delaminated materials ITQ-2 (926 m^2/g) and ITQ-6 (550 m^2/g) were prepared according to previously reported procedures [11a,12,13].

2.5. General procedure for preparing the catalysts

Fifteen milliliters of dry toluene, 1 g of the dehydrated support (MCM-41, ITQ-2, or ITQ-6), and 1.042 g (5.77 mmol) of 3-mercaptopropyl-1,1-dimethoxy-1-methylsilane were added into a round-bottom flask equipped with a reflux condenser and a magnetical stirrer under nitrogen atmosphere. The slurries were heated at reflux temperature for 18 h. The solids were recovered by filtration and washed exhaustively with dichloromethane.

Seven and one-half millimoles of pure complexes (**1**, **2**, or **3**) were added to 10 ml chloroform solutions containing 1 g of mercapto-functionalized solids (MCM-41, ITQ-2, or ITQ-6). The resulting slurries were purged for 10 min with N_2. Then, 25 mg of 2,2′-azobis(isobutyronitrile) (AIBN) was added under nitrogen, and the mixtures were heated to 80 °C for 16 h with stirring. After cooling, the suspensions were filtered, and the pale brown solids were washed exhaustively with CH_2Cl_2.

Silylation of the samples was accomplished as follows: 1 g of the previously loaded solids was suspended in 15 ml of fresh toluene with 0.469 g (2.90 mmol) of silylating reagent, 1,1,1,3,3,3-hexamethyldisilazane (HMDS). The mixtures were heated again at reflux temperature for 2 h, filtered, and washed exhaustively with dichloromethane. The functionalization and silylation degree achieved in each sample were: *MCM-41*: mercapto groups, 1.39 mmol S g^{-1}; trimethylsilyl groups 0.65 mmol g^{-1}. *ITQ-2*: mercapto groups, 0.85 mmol S g^{-1}; trimethylsilyl groups, 0.47 mmol g^{-1}. *ITQ-6*: mercapto groups, 0.66 mmol S g^{-1}; trimethylsilyl groups, 1.2 mmol g^{-1}. The loadings of bounded chiral Mn(III) salen catalysts ranged from 0.013 to 0.096 mmol g^{-1}.

2.6. General procedure for the immobilization of complex 2 and anionic tensioactive molecules

Seven milliliters of dry toluene, 0.72 g of dehydrated pure silica MCM-41, and 5.54 mmol of 3-mercaptopropyl-1,1-dimethoxy-1-methylsilane were added into a round-bottom flask equipped with a reflux condenser and a magnetical stirrer under nitrogen atmosphere. The suspension was heated overnight at reflux temperature. The solid was recovered by filtration and washed exhaustively with dichloromethane (the amount of mercapto groups calculated by elemental analysis was 0.37 mmol g^{-1}). The resulting solid was suspended in 7 ml chloroform solution containing 0.18 mmol of pure complex **2**. The mixture was purged for 10 min with N_2. Then 15 mg of the radical initiator AIBN were added under nitrogen and the mixture was heated to 80 °C for 16 h while stirring. After cooling, the pale brown solid was filtered and Soxhlet extracted with dichloromethane. The resulting solid was suspended in 8 ml dimethylformamide solution containing 5 mmol of 12-bromododecanoic acid and the mixture was heated to 155 °C for 24 h. The solid was recovered by filtration and was washed exhaustively with acetonitrile. The loaded material was treated with 7 ml of 0.05 M NaOH ethanolic solution at room temperature while stirring for 15 min. The resulting solid was filtered and washed exhaustively with acetonitrile.

2.7. General procedure for epoxidations

The reactions were carried out at 0 °C in a system composed of 2 ml CH_2Cl_2 and 2 ml of an aqueous buffered solution of NaOCl as oxidant (pH 11). The reaction solutions contained 1 mmol of olefin, 1 mmol of n-undecane as internal standard, and 0.5 to 5% of Mn(III) salen catalyst. The reactions were monitored by chiral GC chromatography and HPLC.

2.8. Instrumentation

IR spectra of pure complexes were recorded on KBr pellets in a Nicolet 710 FT spectrophotometer. FT-IR spectra of supported complexes were recorded at room temperature using a greaseless quartz cell fitted with CaF_2 windows in a Nicolet 710 FT spectrophotometer. Self-supported wafers (~ 10 mg) were prepared by pressing the zeolite powder at 1 ton cm^{-2}. The samples were outgassed at 100 °C under 10^{-2} Pa for 1 h before recording the IR spectra.

Room-temperature transmission UV–vis spectra of transparent solutions were recorded in a Shimadzu UV–vis scanning spectrophotometer. DR spectra of the opaque powders were recorded in a Varian Cary 5G UV–vis NIR spectrophotometer adapted with a praying mantis attachment and using $BaSO_4$ as reference.

Combustion chemical analysis of the samples were carried out using a Fisons EA 1108-CHNS-O analyzer. FAB MS spectra of the manganese salen complexes were recorded using a VG-Autospec.

2.9. Molecular modeling

Molecular simulations were performed using an atomistic mechanics methodology and Universal Force Field based calculations [17a,b]. The energetic minimizations were carried out with standard techniques as implemented in the software package Cerius 2-4.6 [17c].

3. Results and discussion

Three different preformed Mn(III) salen catalysts were immobilized through a similar anchoring method on the surface of mesoporous MCM-41 (pure silica; diameter pore 38 Å) and pure silica delaminated materials ITQ-2 and ITQ-6 provided a large external surface and large amount of available silanol groups on these structured materials [11–13]. Effectively, ITQ-2 consists of very thin silica layers 2.5 nm in height organized in a "house of cards"-type structure. This material (prepared by delaminating the precursor of the pure siliceous MWW zeolite) contains a very large and well-defined external surface ($> 800\ m^2\ g^{-1}$), whereas ITQ-6 (a delaminated material derived from the lamellar precursor of the ferrierite zeolite) has a total surface area greater than $500\ m^2\ g^{-1}$ [12,13]. In this respect, both type of supports (having an important population of silanol groups highly accessible) are clear candidates for anchor metal precursors or transition metal complexes with high levels of dispersion on the surfaces.

In the first stage we prepared the vinyl monomer [(R,R)-N,N'-bis(3-*tert*-butyl-5-vinylsalycilidene)-1,2-cyclohexanediamine] manganese(III) chloride (**1**) by following the synthetic sequence shown in Scheme 1 (see Section 2). Characterization of pure complex **1** by IR spectroscopy showed the characteristic IR vibration bands of unsupported Mn(III) salen complexes, i.e., the imine stretching vibration around $1630\ cm^{-1}$ and the typical band of metallosalen complexes at $1540\ cm^{-1}$. On the other hand, the electronic absorption spectrum in dichloromethane solution showed typical ligand transitions of the brownish oxidized complex at 225, 275, and 340 nm and a weak d–d transition around 500 nm. Once established, the identity of the complex, compound **1**, was covalently linked to the surface of MCM-41 through radical addition of mercapto groups placed previously in the solid by using azoisobutyronitrile as radical initiator (see Scheme 1 and details on this preparation under Section 2). In this case the FT-IR spectrum of the resulting supported complex (**1**–MCM41) exhibited very weak and undefined bands; herein only the UV–vis spectra in diffuse reflectance mode showed the typical unfeatureless spectra associated with these types of Mn(III) salen complexes (Fig. 1).

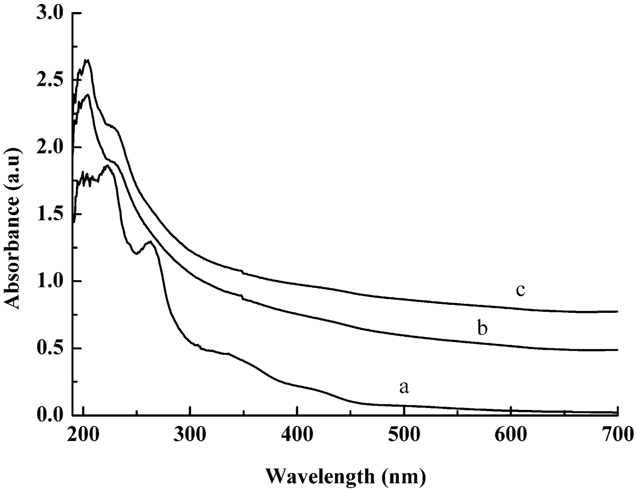


Fig. 1. DR–UV spectra of complexes **1**, **2**, and **3** supported on pure silica MCM41 and silylated ITQ-6: (a) **1**–MCM41; (b) **2**–MCM-41; (c) **3**–ITQ-6s.

The efficiency of **1**–MCM41 as catalyst was tested in the epoxidation reaction of 1-phenylcyclohexene and showed good activity (conversion of 72%, which corresponds to a TON of 29), moderate levels of selectivity (75%), and very low levels of stereoinduction (8% ee) at 0 °C (see entry 1 in Table 1). As the existence of residual amounts of uncomplexed Mn(III) that could be catalyzing the reaction in a nonselective way is a priori not possible because the complex was completely built up before the anchoring, the possibility that the steric and electronic properties of the salen framework could be unfavorably altered by the replacement of two bulky *tert*-butyl groups on both aromatic portions is not unrealistic. In fact, in previous literature references on the epoxidation reaction mechanism it has been suggested that the alkene approaches the oxygen at the oxomanganese(V) intermediate in a "side-on" orientation to avoid steric interactions with the bulky *tert*-butyl substituents [1a,14]. Hence, it is very likely that any structural change involving these substituents at the respective aromatic positions may alter the enantioselectivity values that can be achieved with *tert*-butyl substituents.

Taking into account these premises, we devised the preparation of a new supported chiral manganese complex with the anchoring point located away from the stereogenic center. This complex would maintain the four crucial *tert*-butyl substituents at the near-planar salen ligand having simultaneously a terminal double bond on the monodentate ligand at the axial position (see Scheme 2). Moreover, we speculated on the possibility that the introduction of a longer spacer between the solid and the metal center (in the form

Table 1
Results on the catalytic asymmetric epoxidation of alkenes with chiral manganese(III) salen complexes **1**, **2**, and **3** supported on MCM-41 and delaminated zeolites ITQ-2 and ITQ-6

Substrate[a]	Catalyst	Time (h)	Conversion[b] (%)	Epoxide selectivity[b] (%)	ee[b] (%)	TON[c]
1-Phenylcyclohexene	**1**–MCM41[d]	19	72	75	8	29
	2–MCM41[d]	23	89	78	86	36
	2–MCM41[e]	29	66	66	76	
	2–MCM41[f]	47	84	60	52	
	2–MCM41t[d,g]	66	93	16	46	37
	3–MCM41s[h]	48	99	82	70	21
	2–ITQ-2s[h]	47	98	90	81	20
	2–ITQ-2s[e,h]	48	73	80	63	
	2–ITQ-6s[h]	47	98	90	76	20
Indene	**3**–ITQ-2s[h,i]	48	56	90	62	112
	3–ITQ-6s[h,i]	70	90	90	56	180
1,2-Dihydronaphthalene	**3**–ITQ-2s[h,i]	54	68	85	62	136
	3–ITQ-6s[h,i]	54	89	90	56	178

[a] All reactions were performed at 0 °C by using solid catalysts containing 5% mmol of chiral Mn(III) complex, 1 mmol of alkene, 1 mmol of undecane as internal standard, and NaOCl as oxidant.

[b] Conversion, epoxide selectivity and enantiomeric excess (ee) were determined by capillary GC (Chiraldex G-PN column) and chiral HPLC (Chiraldex OB and OD columns).

[c] Calculated as millimoles of substrate converted per millimole of catalyst.

[d] 2.5% mmol chiral Mn(III) catalyst.

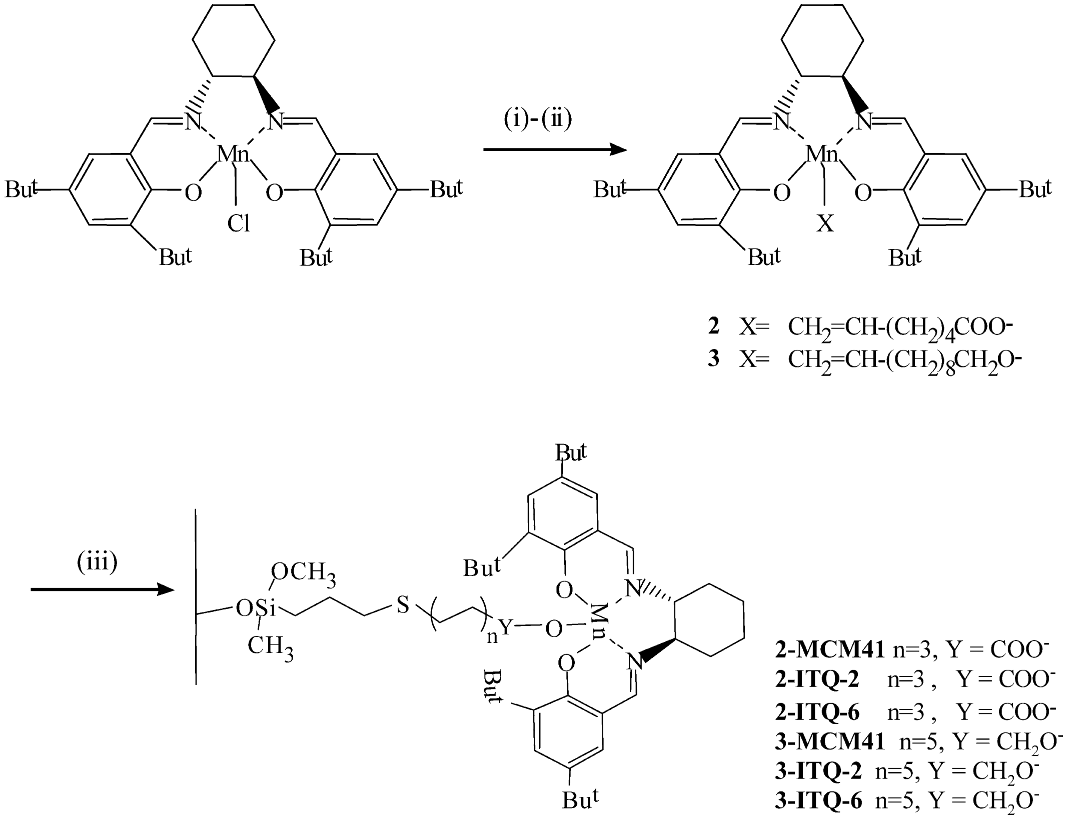
[e] First reuse.

[f] Second reuse.

[g] Tensioactive-containing MCM-41.

[h] Silylated catalysts.

[i] 0.5% mmol of chiral Mn(III) complex.



Scheme 2. Schematic representation of the synthetic procedure followed for the immobilization of pure complexes **2** and **3** on MCM41, ITQ-2, and ITQ-6 materials: (i) $AgClO_4$, CH_3CN; (ii) $CH_2{=}CH–(CH_2)_4COONa$ (or $CH_2{=}CH–(CH_2)_8CH_2ONa$); (iii) MCM-41 (or ITQ-2 or ITQ-6), toluene, reflux.

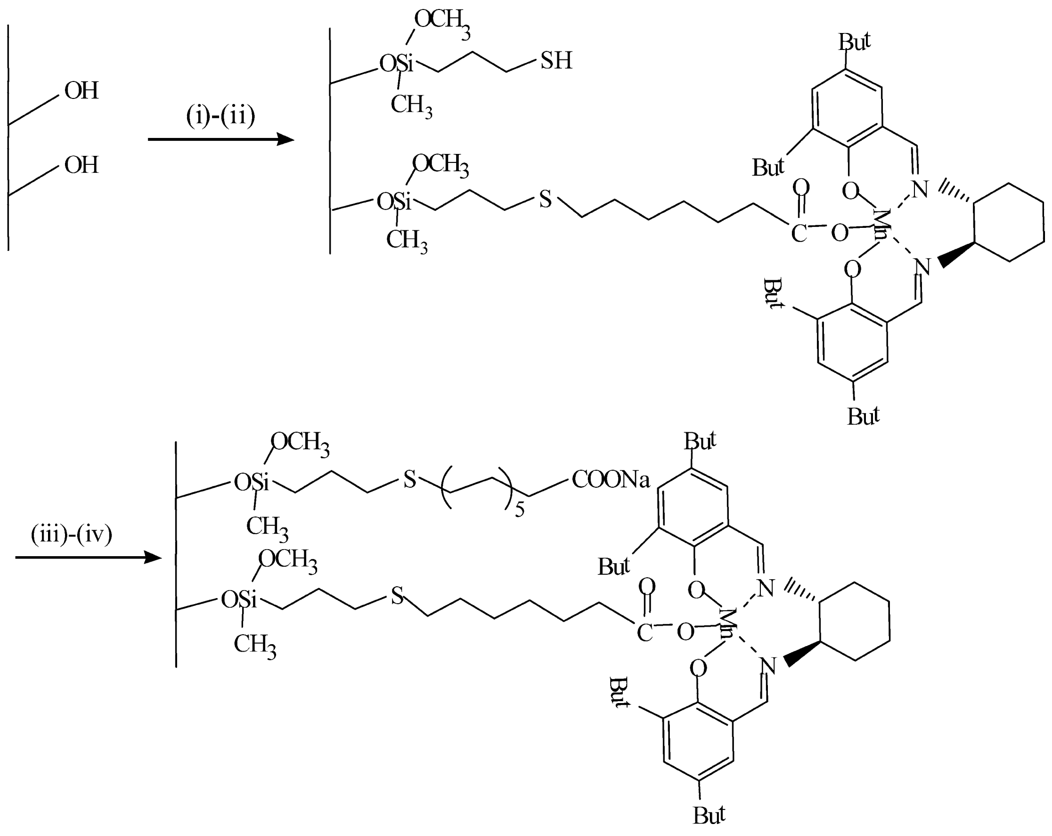
of a long *n*-alkyl chain) would be beneficial for both activity and enantioselectivity, as the existence of less steric hindrance would cause the performance of this catalytic system to approach that of the homogeneous model in the liquid phase [18]. Accordingly we chose the 6-heptenecarboxylate anion as axial coordinating ligand as it had the necessary bifunctionalization for coordinating the metal (the carboxylate group) and carrying out the simultaneous attachment to the solids through the terminal double bond (see Scheme 2).

Thus we prepared the vinyl monomer [(*R*,*R*)-*N*,*N′*-bis(3,5-di-*tert*-butyl-5-salycilidene)-1,2-cyclohexanediamine] manganese(III) 6-heptenecarboxylate (**2**) in a straightforward fashion by methatesis of the chloride ligand of the original Jacobsen catalyst by the 6-heptenecarboxylate anion as outlined in Scheme 2 (details of the procedures, synthetic conditions, and characterization are provided under Section 2).

As in the previous case, the pure complex **2** was covalently linked to the surface of MCM-41 through radical addition of the mercapto groups placed previously on the solid to the terminal double bond on the axial coordinating ligand, hence affording the heterogeneous catalyst **2**–MCM41 as depicted in Scheme 2.

Again the identity of this immobilized complex was established by UV–vis spectroscopy in diffuse reflectance mode (see Fig. 1), whereas its catalytic activity was routinely determined in the epoxidation reaction of 1-phenylcyclohexene. As can be followed from results collected in Table 1, the solid catalyst **2**–MCM-41 gave similar yields of chiral epoxide and very good levels of stereoinduction (see Table 1). The remarkable difference between the chiral inductor characters of the supported catalysts when they are linked through the stereogenic tetradentate salen ligand or, alternatively, through the achiral apical ligand is noticeable and strongly supports the notion that the significant low enantiomeric excess obtained with the supported catalyst **1**–MCM41 is due (at least in part) to the absence of bulky ligands around the active Mn^{3+} ion to create a stereogenic environment (a fact that has been well established for unsupported complexes) [1a,14]. Nevertheless, the existence of unfavorable electronic effects and/or ligand distortion modes that would lead presumably to a loss of the near-planar geometry of the equatorial salen ligand has been recognized early on [15].

On the other hand, in an attempt to facilitate the interaction between the aqueous oxidant ClO_4^- and the heterogeneous complex, we conceived the preparation of metal complex-containing particles with amphiphilic character. These particles contained both the chiral manganese complex **2** and a sort of anionic tensioactive molecule that was immobilized at the surface of pure silica MCM-41 (**2**–MCM41t) (see Scheme 3 and details of its preparation under Section 2). In this case the tensioactive refers to a molecule with a hydrophilic head group (a carboxylate an-



Scheme 3. Immobilization of the anionic tensioactive and pure complex **2** on MCM41: (i) $CH_3Si(OCH_3)_2CH_2CH_2CH_2SH$, toluene, reflux; (ii) **2**, Cl_3CH, AIBN, N_2, reflux; (iii) $BrCH_2(CH_2)_{10}COOH$, DMF, reflux; (iv) 0.05 M NaOH, EtOH.

ion) and a hydrophobic tail group formed by a long n-alkyl chain. We expected that the highly hydrophilic character of the surfactant molecules at the head group would drive the aqueous oxidant to assemble or accumulate at the surface of the solid, favoring interaction between the hypochlorite molecules and the metal. The efficiency of this catalyst was tested in the epoxidation reaction of 1-phenylcyclohexene, giving very low values of selectivity (16%) and moderate levels stereoinduction (46% ee) at 0 °C (see Table 1). This discouraging result can be explained if we take into account that (as has been demonstrated recently) control of hydrophobicity of the heterogeneous surfaces can influence the catalytic activity of a solid catalyst by allowing selective adsorption of reactants and products and therefore favoring, in some cases, secondary reactions [19]. In our case, the preferable selective adsorption of water and/or oxidant-derived species could account for such undesired collateral reactions (vs epoxide ring opening).

Hereinafter anchoring complex **2** on the surface of ITQ-2 and ITQ-6, we accomplished exhaustive silylation of any remaining silanol group (Si–OH) with hexamethyldisilazane (HMDS) to reduce the hydrophilicity of the surfaces to give the heterogeneous complexes **2**–ITQ-2s and **2**–ITQ-6s (see synthetic sequence described in Section 2.5).

In this case the catalytic activity of these solids was determined in the epoxidation reaction of 1-phenylcyclohexene, giving identical TON values, very good yields of chiral epoxides (around 90%), and good levels of stereoinduction (see Table 1). Fig. 2 is a schematic representation of the external surface of delaminated zeolite ITQ-2 and the optimized structural conformation achieved by complex **2** on the surface of this material calculated by using standard techniques as implemented in the software package Cerius 2-4.6 [17].

Finally, following with the same synthetic methodology, a third chiral pentadentate manganese complex was prepared by chloride shifting with 10-undecenoxide anion to give [(R,R)-N,N'-bis(3,5-di-*tert*-butyl-5-salycilidene) 1,2-cyclohexanediamine] manganese(III) 10-undecenoxide (**3**) (see Scheme 2 and Section 2). The resulting pure complex **3** was linked to the surface of mercapto-functionalized MCM41, ITQ-2, and ITQ-6 matrices through the terminal vinyl moiety, affording, after subsequent silylation, the heterogeneous complexes **3**–MCM41s, **3**–ITQ-2s, and **3**–ITQ-6s (see Section 2). The DR–UV spectra of these three solid catalysts were rather similar. For this reason, Fig. 1 shows the UV spectrum of only one of these supported catalysts (**3**–ITQ-6s) recorded in diffuse reflectance mode. In addition, Fig. 2 shows the optimized structural conformation achieved by complex **3** on the surface of ITQ-2 according to the Cerius 2-4.6 program.

These three new supported complexes were used as catalysts in the epoxidation reaction of prochiral 1-phenylcyclohexene, 1,2-dihydronaphthalene, and indene with excellent selectivities and good levels of stereoinduction (see Table 1). It is necessary to point out that the good activity and selectivity parameters achieved in the epoxidation of 1,2-dihydronaphthalene and indene were accompanied by the highest TON values, as the amount of catalyst employed in these cases was the smallest (see Table 1).

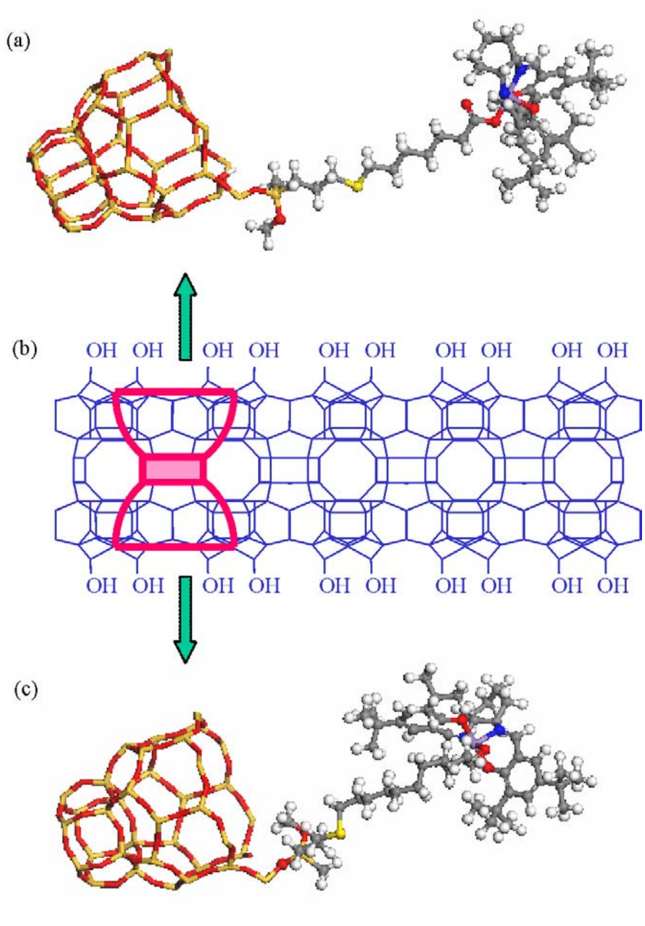


Fig. 2. (a) Molecular simulation of manganese salen complex **2** anchored to the ITQ-2 surface. (b) Schematic representation of the external structure of ITQ-2, which is composed of an array of cups containing silanols in specific positions. (c) Computational simulation of manganese salen complex **3** grafted onto the ITQ-2 surface.

Finally, because the reusability of the complexes anchored or fixed on a support is one of the most important advantages of heterogeneization, the solids **2**–MCM41 and **2**–ITQ-2 were separated by filtration, washed with fresh solvent, and recycled. Then, two new epoxidation reactions were repeated with both catalysts by adding 1-phenylcyclohexene and oxidant NaOCl under the same experimental conditions. Sixty-six percent conversion was achieved after 29 h with only a slight to moderate loss of activity and enantioselectivity in the case of **2**–MCM41, whereas catalyst **2**–ITQ-2 afforded 73% conversion after 48 h, also with a moderate loss of selectivity and enantioselectivity (see Table 1).

In addition, the electronic spectrum of the reused catalyst **2**–MCM41 was recorded and compared with the DR spectrum of the initially loaded material **2**–MCM41, both spectra being qualitatively very similar (not shown). This fact supports the notion that the supported Mn(III) salen complex is not substantially altered under these experimental conditions as confirmed by the relatively good activity and selectivity parameters that could be achieved in a first reuse. In a further experiment the recovered catalyst **2**–MCM41 was reused again in a new catalytic reaction (second reuse). In this case the activity and stereoselectivity of the catalyst declined, although the epoxide was still formed (see Table 1).

In view of these results it can be concluded that this methodology is reasonably effective for improving the retention of the monomeric manganese salen complexes to the supports and allowing the subsequent recycling, whereas the stability of the complexes under oxidizing conditions is also reasonably good as the performance of the heterogeneous catalysts smoothly decreases with time, being more pronounced after prolonged reaction times or subsequent reuses.

4. Conclusion

The preparation of three different Mn(III) salen complexes supported on pure silica mesoporous material MCM-41 and two pure silica delaminated zeolites ITQ-2 and ITQ-6 is reported. The complexes were structurally modified (with respect to the original Jacobsen catalyst) to get the necessary bifunctionalization to carry out the simultaneous attachment to the organic supports and coordination or interaction with metals. These transition metal complexes had a vinyl functionality placed strategically at the equatorial and axial positions of the pentacoordinated manganese complex, respectively. This vinyl moiety served to attach the complex covalently to the supports. In principle, the attachment of the complex through the equatorial position of the metal complex led to a strong reduction in enantioselectivity. Two new chiral manganese salen complexes bearing a vinyl group at the apical coordinating ligand were prepared. These chiral manganese salen complexes, which were fixed to the respective supports through the axial coordinating ligand, were active and more enantioselective toward epoxidation of various prochiral alkenes.

On the other hand, when recycling, the performance of the supported Mn(III) salen catalysts declined, although the epoxide was still obtained with good values of activity and enantioselectivity, especially with the first reuses.

Finally, silylation of the surfaces improved the epoxide selectivity due to reduction of undesirable secondary reactions caused by the selective adsorption of different products on the hydrophilic surfaces.

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