Jacobsen's catalyst anchored on Al-MCM-41 and NH$_2$ group modified Si-MCM-41 as heterogeneous enantioselective epoxidation catalyst using in situ generated dimethyldioxirane as oxidant

Catalizador de Jacobsen inmovilizado en Al-MCM-41 y en Si-MCM-41 modificada con grupos amino y su actividad en la epoxidación enantioselectiva heterogénea utilizando dimetildioxirano generado in situ como oxidante

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Abstract

The enantioselective epoxidation of three prochiral olefins over Jacobsen's catalyst immobilized on Al-MCM-41 and NH$_2$-Si-MCM-41 in the presence of *in situ* generated DMD as the oxygen source was investigated. Experimental results indicate that the catalyst did not significantly suffer any change in its chemical structure. Therefore, the reusability of catalyst could be successfully achieved when it was immobilized by chemical bonding of the salen ligand.

---------- *Key words*: Enantioselective epoxidation, Jacobsen's catalyst, Immobilized catalyst, *in situ* generated DMD, catalyst degradation, recyclability.

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Resumen

En este trabajo se investigó la actividad catalítica del catalizador de Jacobsen inmovilizado en Al-MCMC-41 y en NH_2-Si-MCM-41 en la epoxidación enantioselectiva de tres olefinas proquirales, utilizando dimetildioxirano generado in situ como agente oxidante. Con este agente oxidante, el catalizador no sufrió cambios significativos en su estructura química. El catalizador se reutilizó exitosamente, cuando se inmovilizó por enlace químico covalente a través del ligando de salen.

---------- *Palabras clave*: Epoxidación enantioselectiva, catalizador de Jacobsen, catalizador inmovilizado, DMD generado in situ, degradación del catalizador, reutilización.

Introduction

The enantioselective epoxidation of olefins has received major attention since the corresponding chiral epoxides have become important building units for the synthesis of fine chemicals, drugs, agrochemicals and food additives [1]. In particular, considerable successes through the development of metal-catalyzed oxo-transfer processes have appeared [2, 3, 4]. Chiral manganese (III) salen complexes, developed by Jacobsen and Katsuki, have shown to be highly active and enantioselective for a number of conjugated unfunctionalized olefins [5]. Among them, the general catalyst depicted in figure 1 (well known as Jacobsen's catalyst) has given the best results when using *cis*-disubstituted and cyclic olefins as substrates [6].
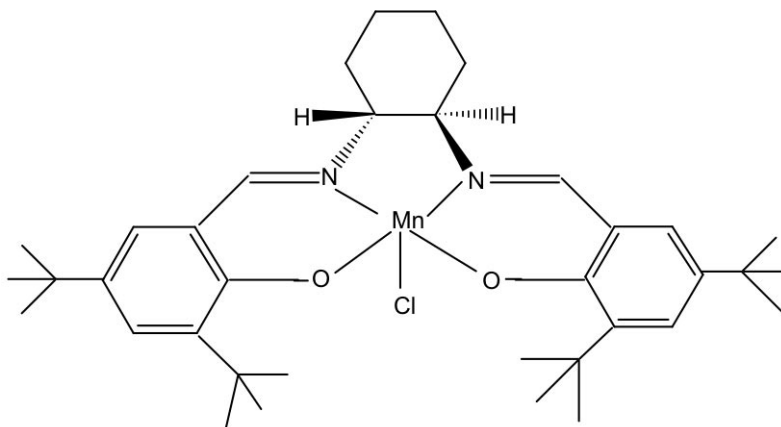

Figure 1 (R,R)-(-N,N'-bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediamine manganese(III) chloride (Jacobsen's catalyst)

Sodium hypochlorite [7], *meta*-chloroperbenzoic acid (*m*-CPBA) [8] and iodosylbenzene (PhIO) [9] are commonly used as the oxygen sources. Additionally, a nitrogen cyclic compound is used to avoid the formation of inactive dimeric μ-oxo manganese (IV) species [6]. For example, 4-phenylpyridine N-oxide (4-PPNO) is a suitable additive in an aqueous-organic biphasic reaction medium, whereas N-methylmorpholine (NMO) is frequently used in an organic phase [10]. Dichloromethane and acetonitrile are the solvents commonly applied [11]. Low reaction temperatures (-70 to 5 °C) have a favorable effect on enantioselectivity [8]. In spite of the excellent catalytic behavior of Jacobsen type catalysts, their productivities (TON) remain low due to

degradation of the salen ligand under prolonged oxidative conditions [12, 13]. One way to improve the catalyst's TON is to try to recycle it. Therefore, many efforts have been made to heterogenize Jacobsen type catalysts, either by using an inorganic or organic matrix as support material [14].

Generally, inorganic supports are mechanically and thermally more stable [15]. Among them, silicious mesoporous materials having the MCM-41 structure with or without framework aluminium have mainly been used [16]. This choice is based on its large pore size (40 Å), which allows the accommodation of bulky organometallic complexes without any hindrance into its porous system [17].

On the other hand, Jacobsen's catalyst is too large to fit into the cavities of faujasite type zeolites, preventing its immobilization according to the "ship-in-a-bottle" concept [18]. Although mesopores can be created by dealumination processes, unremoved extra-framework material can block the access to the open cavities of modified zeolites [19]. Additionally, the remaining pore volume after the immobilization is small, which can affect the diffusion both of reactants and products. Additionally, the effect of catalyst confinement into the support can affect the suitable geometric conformation what the catalyst adopts in homogeneous phase. Thus, poor asymmetric induction is generally observed [18, 20]. An important feature of M41S type mesoporous materials is the presence of free surface silanol groups (SiOH), which are highly accessible to the common silylating agents [21]. Thus, they provide a convenient modification for the immobilization of the catalyst by covalent bonding [22]. On the other hand, the negative charge, generated by the presence of framework aluminum in Al-MCM-41, allows the immobilization of catalyst such as cationic complexes by electrostatic interaction [23]. However, the interaction between the catalyst and the framework anionic center is considered to be very weak, therefore leaching can be expected, depending upon the reaction conditions [15]. Also, the catalyst cannot be encapsulated since the pores of the one-dimensional large pore system of MCM-41 are directly connected to the external surface [24].

Various immobilization methods by covalent attachment have proven to be very stable towards leaching [15, 25]. However, the oxidative degradation of the catalyst in the presence of the usual oxidation agents has limited its reuse [25]. No results for reducing the severe oxidation conditions have been published so far, although steps such as the slow addition of the oxygen source, the use of very low reaction temperatures or short reaction time have been investigated [15].

Dimethyldioxirane (DMD) obtained from Oxone® ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) and acetone has been used in combination with Jacobsen's catalyst for the enantioselective homogenous epoxidation of isoflavones and various 2,2-dimethyl-2H-chromene derivatives [26, 27]. This oxidation agent is prepared *in situ* during the reaction by careful control of the pH in the range 7.0-7.5 [28]. This protocol can be applied in asymmetric epoxidation reactions in order to reduce the prolonged oxidative conditions due to the oxidizing agent.

To evaluate the activity and recyclability of the catalyst under reaction conditions, the enantioselective epoxidation of different types of conjugated olefins with the Jacobsen's catalyst immobilized on either Al-MCM-41 [29] and NH_2 group modified Si-MCM-41 [30], [31], using *in situ* generated DMD as the oxygen source was investigated [28].

Experimental

(1R,2R)-(+)-1,2-diaminocyclohexane-L-tartrate, 3,5-di-tert-butyl-2-salicylaldehyde, 4-tert-butylphenol, dry silver perchlorate, manganese (II) acetate tetrahydrate, lithium chloride, 3-aminopropyltrietoxysilane (3-APTES), styrene, 1,2-dihydronaphthalene, sodium bicarbonate, Oxone® (also known as Caroate: $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$), 4-phenylpyridine-N-oxide (4-PPNO) and anhydrous solvents were purchased from Aldrich. [(R,R)-(–)-N,N'-bis(3,5-di-tert-butylsalicylidene)cyclohexane -1,2-diamines] (Jacobsen's salen) and [(R,R)-(–)-N,N'-bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediaminomanganese(III) chloride] (Jacobsen's catalyst) were prepared according to Jacobsen et al. [32], 2,6-diformyl-4-tert-butylphenol according to Chang et al. [33] and *cis*-ethyl cinnamate according to Jacobsen et al. [34] were synthesized.

To evaluate the enantiomeric excess of the chiral epoxides derivated from *cis*-ethyl cinnamate, a commercial sample of its racemic epoxide

3-ethyl phenyl glycidate (Aldrich, *cis/trans* = 10/90) was used. For the case of styrene and 1,2-dihydronaphthalene, their chiral epoxides were prepared by reaction with *m*-CPBA/NMO in CH_2Cl_2 (substrate/ *m*-CPBA = 1/1, *m*-CPBA/ NMO = 0.5 in 4 ml CH_2Cl_2) at room temperature for 30 min. (R)-styrene oxide was obtained by using (R,R)-Jacobsen' catalyst, while (S)-styrene oxide by using (S,S)-Jacobsen' catalyst. (1S,2R)-1,2-dihydronaphthalene oxide was obtained by using (R,R)-Jacobsen' catalyst, while (1R,2S)-1,2-dihydronaphthalene oxide by using (S,S)-Jacobsen' catalyst.

Al-MCM-41 and Si-MCM-41 were prepared by conventional methods [16, 35]. The materials were dried overnight in vacuum at 413 K and then stored under argon.

Catalyst preparation

Immobilization by ion exchange (method 1)

A method similar to Hutchings et al. [29] was adopted (see figure 2). 3 g Al-MCM-41 was ion exchanged three times with 100 ml of a 0.2 M $Mn(CH_3CO_2)_2.4H_2O$ aqueous solution (100 ml) afterwhich the material was calcined for 6 h at 823 K. This material was denoted Mn-Al-MCM-41. Dry Mn-Al-MCM-41 was treated with 0.82 g Jacobsen's salen in 20 ml dry refluxing CH_2Cl_2 under argon for 24 h. Subsequently, argon was replaced by flowing air and stirring was continued for 6 h. Then, the solvent was removed under reduced pressure at room temperature. The solid was Soxhlet extracted with CH_2Cl_2. The obtained material was denoted MCM1HC.
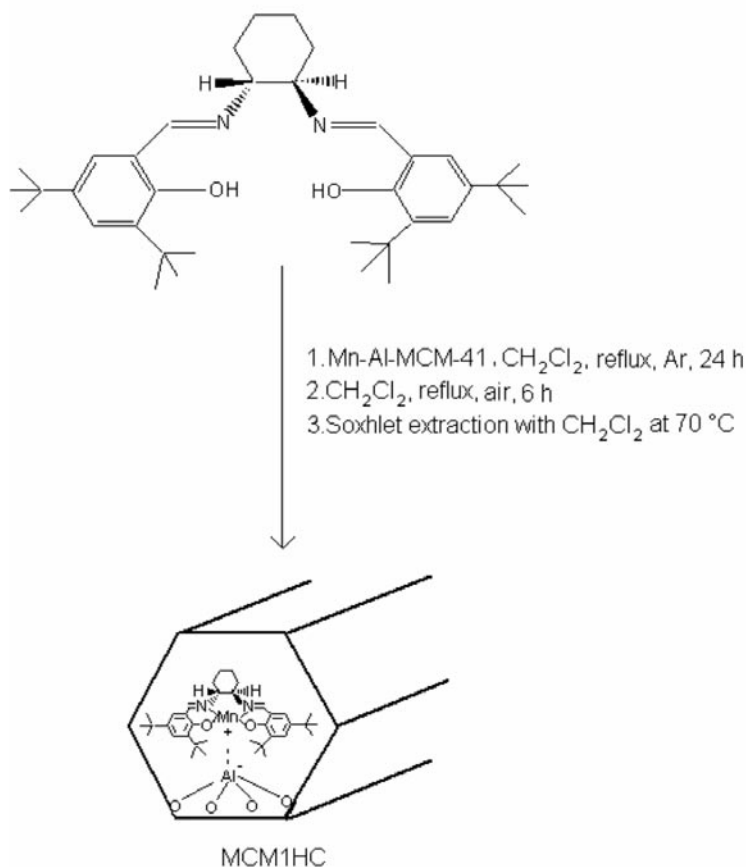

Figure 2 Immobilization by ion exchange

Immobilization by coordination bonding (method 2)

A method similar to García et al. [30] was used (see Figure 3), in which Si-MCM-41 is functionalized with 3-APTES by adding 5 g Si-MCM-41 to a solution containing of 1.84 g 3-APTES dissolved in 15.33 g dry toluene. The suspension was refluxed under argon for 24 h and subsequently Soxhlet extracted with CH_2Cl_2 for 24 h. The thus obtained solid was dried at 318 K under vacuum and denoted NH_2-Si-MCM-41.
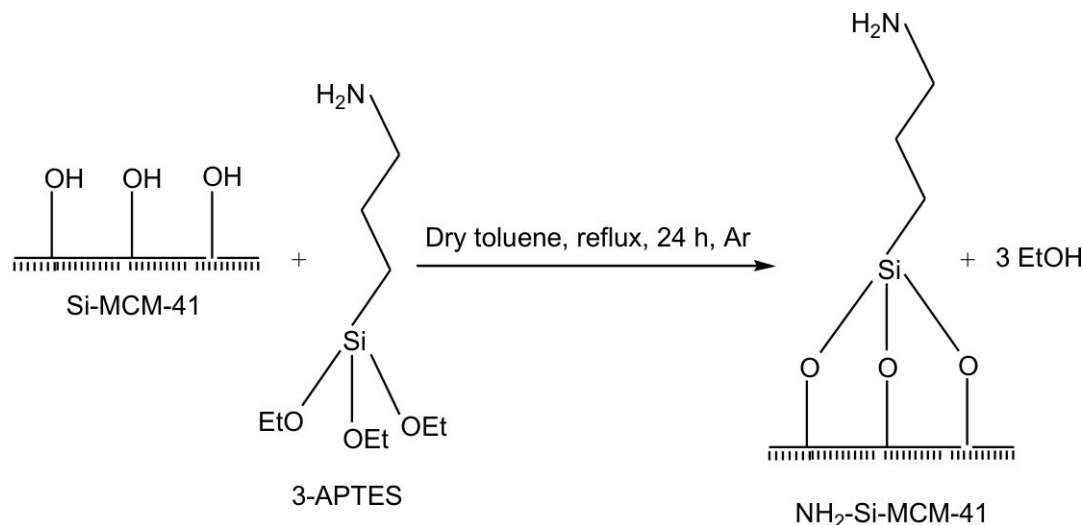

Figure 3 Aminopropyl functionalized Si-MCM-41

5.30 g **Jacobsen's** catalyst was mixed with 1.73 g $AgClO_4$ in 25 ml dry CH_3CN at room temperature for 16 h. After filtration through Celite and washing with dry CH_3CN, the filtrate was concentrated under reduced pressure. Dry CH_2Cl_2 and NH_2-Si-MCM-41 were added and stirred at room temperature under argon for 24 h. The solid was Soxhlet extracted with CH_2Cl_2. The obtained material was denoted MCM2HC. Figure 4 depicts the preparation method.

Immobilization by chemical bonding on amino propyl functionalized Si-MCM-41 (method 3)

A method similar to Kim et al. [31] was adopted (see figure 5). 3 g Si-MCM-41 was reacted with 0.30 g 2,6-diformyl-4-tert-butylphenol and 0.38 g (1R, 2R)-(+)-1,2-diaminocyclohexane in refluxing dry ethanol for 14 h under argon. After cooling, the material was filtered, washed with CH_2Cl_2 and methanol and dried under vacuum. The obtained solid NH_2-MCM-41(1), was treated with 0.34 g 2,4-di-tert-butyl salicylaldehyde in refluxing dry ethanol for 18 h under argon. The resulting material (NH_2-MCM-41(2)) was treated with 0.36 g $Mn(CH_3CO_2)_2.4H_2O$ and 0.062 g LiCl in ethanol at 343 K under air for 4 h, exposed to vacuum and Soxhlet extracted with CH_2Cl_2. The obtained material was denoted MCM3HC.

Catalyst Characterization

Synthesized materials were characterized by XRD (Siemens D-500), N_2 sorption (ASAP 2010 Micromeritics): the support materials were evacuated at 673 K and 10^{-2} Pa for 12 h, whereas the heterogenized catalysts were treated at 373 K and ICP-AES (spectroflamed; typically, 30 mg sample was dissolved in 500 μl 40% HF solution, 4 ml 1:4 H_2SO_4 solution and 45 ml H_2O), TG/DSC was performed on a Netzsch 209/2/E
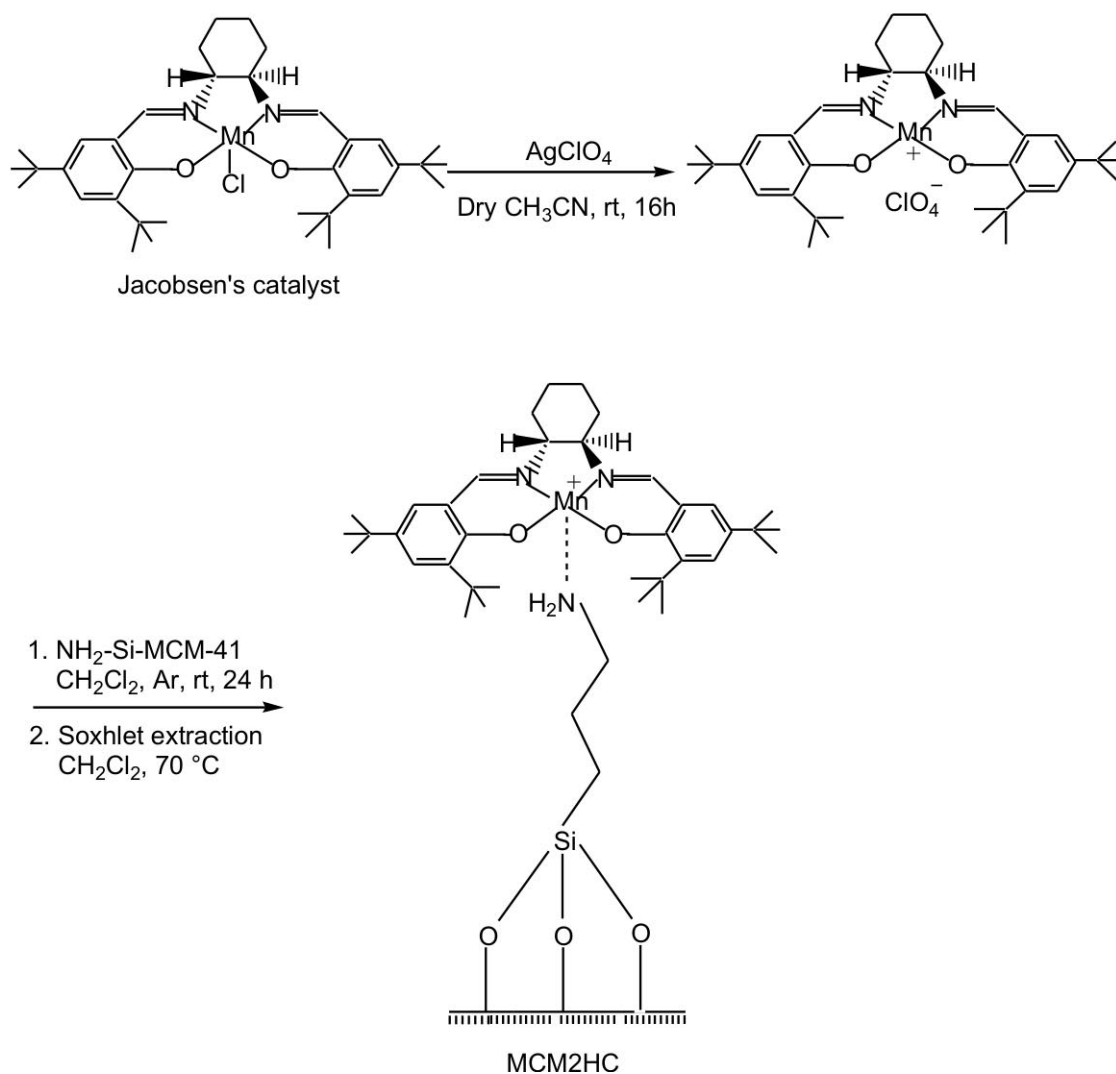
Figure 4 Anchoring of Jacobsen's catalyst on NH$_2$-Si-MCM-41 through the manganese ion

equipped with a STA 409 controller. The heating rate was 2 K/min from 298 to 1273 K, using Al$_2$O$_3$ crucibles; α-Al$_2$O$_3$ was used as reference material. FTIR spectra was collected on a Nicolet Protégé 460 and diffuse reflectance (DR) UV-VIS spectra on a Perkin Elmer Lambda 7.

Catalytic testing

4 ml Acetone was added to a mixture of 0.25 mmol olefin (styrene, *cis*-ethyl cinnamate or 1,2-dihydronaphthalene), 0.075 mmol 4-PPNO, 1.2 mmol NaHCO$_3$ and catalyst (0.06 mmol homogeneous or 300 mg heterogenized catalyst). Subsequently, a solution of 0.25 mmol Oxone® (2KHSO$_5$•1KHSO$_4$•1K$_2$SO$_4$) in 4 ml water was added over 20-40 minutes under continuous stirring, controlling the pH between 7.0-8.0 with aqueous NaHCO$_3$ (5 %wt, pH = 8.0). The reaction was stopped and the catalyst renoved. The liquid was extracted with CH$_3$CO$_2$C$_2$H$_5$ and the aqueous phase was separated. The organic
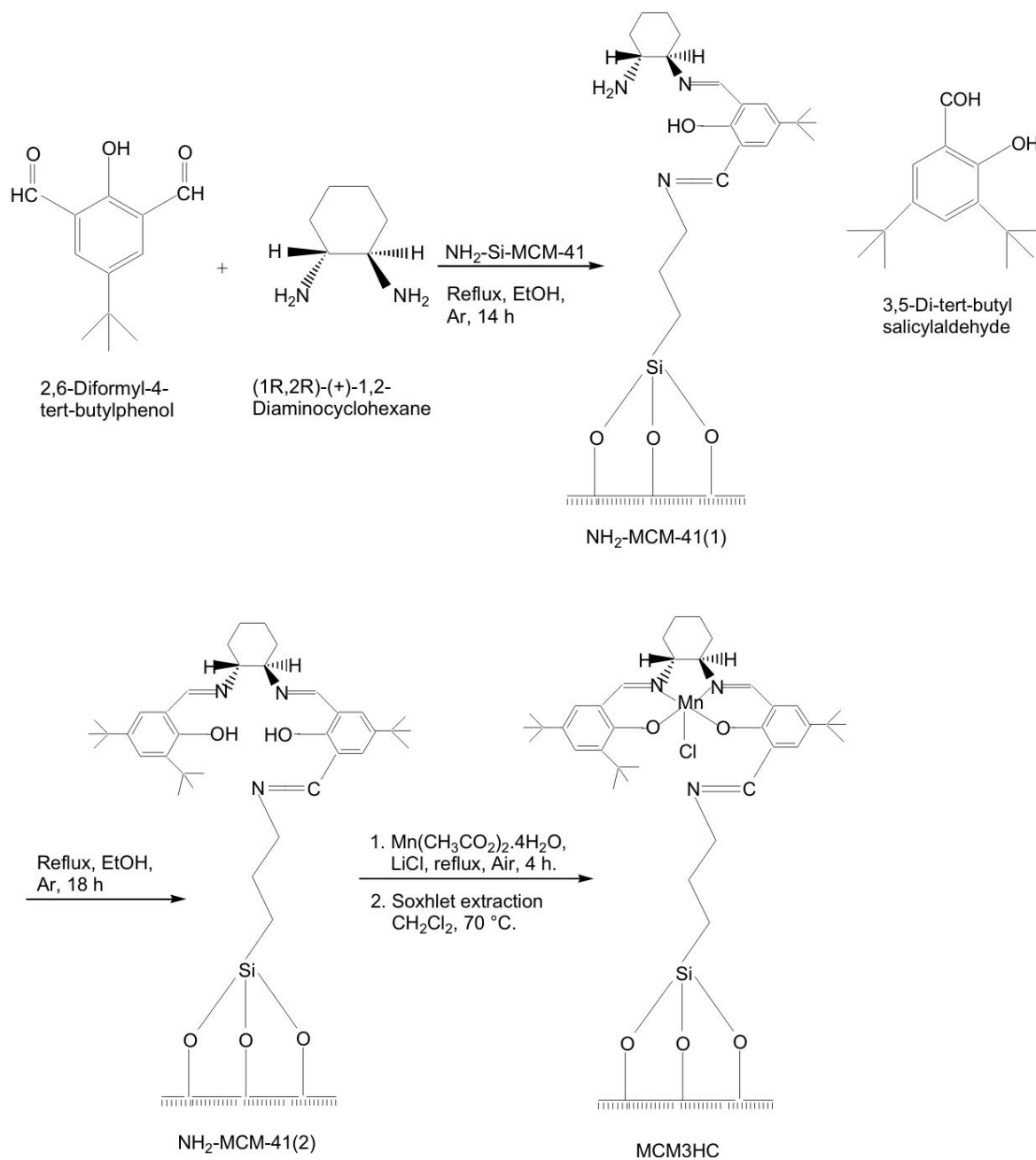
Figure 5 Anchoring of Jacobsen's catalyst on NH_2-Si-MCM-41 via covalent bonding of the ligand to the linker

phase was analyzed with GC on a column γ-chiraldex and the Mn content with ICP-AES. The recovered catalyst was washed with sufficient H_2O for 24 h to remove inorganic salts resulting from Oxone® ($KHSO_4$ and K_2SO_4) and the buffer solution ($NaHCO_3$). Finally, the catalyst was Soxhlet extracted with CH_2Cl_2 for 24 h and dried at room temperature prior to reuse.

Results and discussion

Catalyst characterization

The XRD pattern of Al-MCM-41 and Si-MCM-41 were similar to those reported in literature and could be hexagonally indexed. After the immobilization using different procedures all materials showed a reduction in both the surface area and pore volume (see table 1), which was an indication that the organometallic complex was mainly located inside the mesopores of the support [24]. Furthermore, the reduction in both surface area and mesopore volume increased with the number of steps in the immobilization process. Thus, when the catalyst was ionically bonded to the carrier without modification in the salen ligand and the support (MCM1HC), a considerable pore volume was still present for the catalytic process, whereas for the other two materials (MCM2HC and MCM3HC) a stronger reduction was observed (see table 1). However, in the other cases the remaining pore volume was considerably larger than those commonly reported for zeolites [18, 20].

Table 1 Nitrogen sorption data of different materials

Material	BET surface area (m^2/g)	BJH pore volume (cm^3/g)
Al-MCM-41	981	0.978
MCM1HC	890	0.550
Si-MCM-41	968	0.685
NH$_2$-MCM-41	408	0.260
MCM2HC	332	0.100
MCM3HC	237	0.041

The loading of immobilized catalyst was estimated from the manganese content determined by ICP-AES and the salen ligand content determined by TGA (see table 2). For that material obtained from **method 2** (MCM2HC), loading was determined from the manganese content, since the homogeneous catalyst was prepared prior to the immobilization process. Samples obtained both by treatment of the salen ligand on Mn modified Al-MCM-41 (MCM1HC) and building up the salen ligand (MCM3HC) revealed an excess of manganese. Although the amount of the salen ligand was increased (by maintaining constant the manganese content) to reduce the free manganese atoms, the Mn/salen ratio did not vary significantly, which indicates that some Mn sites in or on the mesoporous structure are not readily accessible for the salen ligand. Another possibility to reduce the Mn/salen ratio to about 1 is to reduce the amount of manganese, but in this way the catalytic activity might be reduced, too. On the other hand, the difference in catalyst loading could be due to the difference in preparation method.

The materials were furthermore investigated by FT-IR and DR UV-Vis. Figure 6 shows the FT-IR spectra for the Jacobsen's salen, Jacobsen's catalyst, the Al-MCM-41 carrier and the heterogeneous catalyst MCM1HC. The C=N imine vibration signal of the salen complex at 1630 cm^{-1} shifts to lower wavenumbers [36] upon complexation with the metal (c.a 1610 cm^{-1}). Unfortunately, this signal could not be used to evaluate the immobilization process, as the Al-MCM-41 support shows a broad signal centered at 1640 cm^{-1}, attributable to H$_2$O in inorganic materials [13]. The most characteristic signal

Table 2 Analytical characterization

Catalyst	Mn loading[a] (mmol/g)	Salen loading[b] (mmol/g)	Mn/salen[c] (mmol/mmol)	Complex loading (mmol/g)
MCM1HC	0.228	0.089	2.561	0.089[d]
MCM2HC	0.035	N. D.	1.000	0.035[e]
MCM3HC	0.439	0.134	3.276	0.134[d]

a Determined by ICP-AES. b Determined by TGA. c Molar ratio. d Calculated from the salen ligand content. e Calculated from the Mn content. N. D.: not determined.
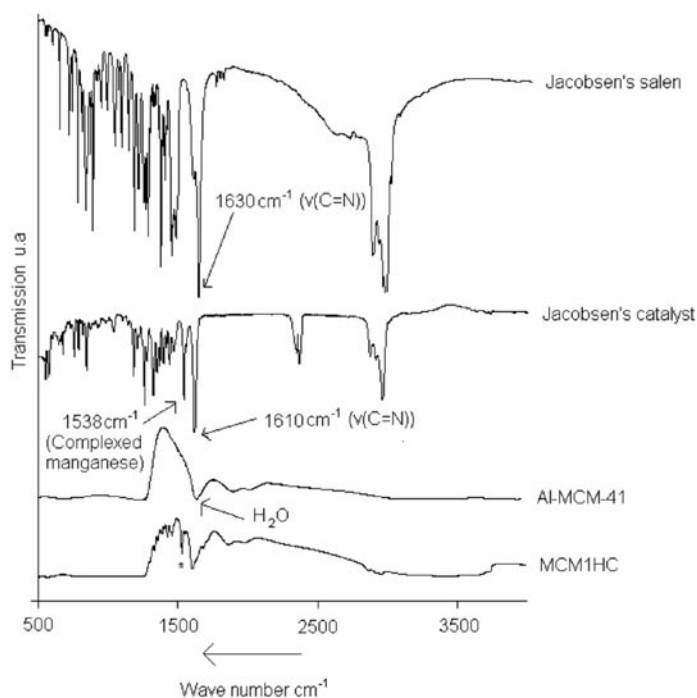
Figure 6 FT-IR spectra of the Jacobsen's catalyst and the Jacobsen's catalyst immobilized by ionic bond

from the structure of metal salen complexes is the presence of a band near 1540 cm⁻¹ [24]. This signal was found in the spectra of sample MCM1HC (indicated as "*" in figure 6), which is an indication that Jacobsen's catalyst did not suffer any change in its chemical structure during the immobilization process (see figure 7).

The signal attributable to the metallosalen complex could not be clearly observed in the spectra of MCM2HC and MCM3HC because several signals originating from amino propyl groups appeared in the same area in the IR spectra (1450-1560 cm⁻¹). Here DR UV-Vis was chosen for the characterization (see figure 7). The UV-Vis spectra of Jacobsen's salen showed typical bands near at 260 and 330 nm, attributable to ligand n'–π* and π–π* charge transfer bands [37]. Jacobsen's catalyst exhibited a broad signal centered around 425 nm, attributable to the ligand-to-metal charge transfer band,
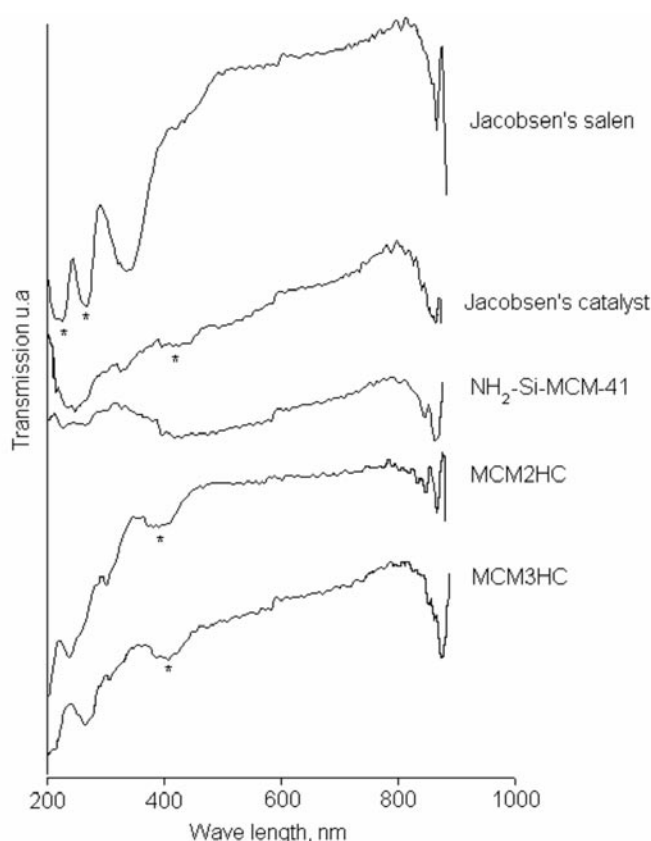
Figure 7 UV-Vis spectra of Jacobsen's catalyst and Jacobsen's catalyst immobilized on NH_2 group modified Si-MCM-41

similar to metallosalen compounds [37]. After immobilization this signal appeared with lower resolution than for the homogeneous catalyst. The UV-Vis spectra of the heterogenized catalysts were very similar to that of the free Jacobsen's catalyst, revealing that the organomanganese complex was present in or on the mesoporous structure.
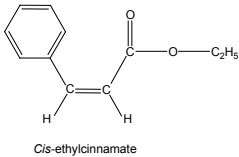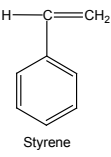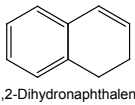
Catalytic activity

The results of catalytic experiments are presented in table 3. In the absence of catalyst, racemic epoxidation was observed for all substrates. Furthermore, control experiments did not demonstrate any catalysis by either uncomplexed manganese or the supports (Al-MCM-41 or NH_2-

Si-MCM-41). The use of CH_2Cl_2 or CH_3CN instead of acetone resulted only in a poor asymmetric epoxidation (conversions of up to 5 %), demonstrating that the *in situ* formation of DMD lead to the formation of the oxo-manganese(V) oxidation active species.

The difference in conversions and enantioselectivities for a given catalyst depended on the nature of the olefin. Thus, *cis*-ethyl cinnamate, an unreactive olefin (electron poor substrate), afforded the highest enantioselectivities than those substrates which are more easily oxidized (styrene and 1,2-dihydronaphthalene). In comparison with the homogeneous catalytic activity, the heterogenized catalyst showed only a slight reduction *cis*-ethyl cinnamate conversion, whereas similar conversions

Table 3 Catalytic activity for the enantioselective epoxidation of three representative olefins[a].
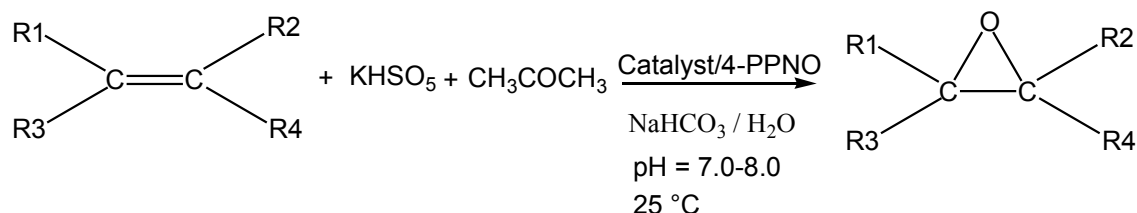
Substrate	Catalyst	Conversion[b] %	Selectivity[b] %	(ee) [d, i] %
Cis-ethylcinnamate	Homogeneous	38	99 (5.0)[c]	86[e] (72)[f]
	MCM1HC	32	97 (5.0)[c]	75[e] (50)[f]
	MCM2HC	25	98 (4.7)[c]	78[e] (60)[f]
	MCM3HC	30	95 (4.5)[c]	35[e] (30)[f]
Styrene	Homogeneous	100	100	40[g]
	MCM1HC	100	100	38[g]
	MCM2HC	95	100	35[g]
	MCM3HC	97	100	12[g]
1,2-Dihydronaphthalene	Homogeneous	94	89	37[h]
	MCM1HC	95	88	32[h]
	MCM2HC	96	90	34[h]
	MCM3HC	95	90	8[h]

a Reaction conditions: Substrate = 0.25 mmol; Oxone® (2 $KHSO_5 \bullet KHSO_4 \bullet K_2SO_4$) = 0.25 mmol; catalyst = 30 mg homogeneous or 300-500 mg heterogoneous catalyst; 4-PPNO = 0.075 mmol; CH_3COCH_3 = 4 ml; $NaHCO_3$ = 3.5 mmol; T = 23-25 °C; the pH was maintained between 7.0 and 8.0 with aqueous $NaHCO_3$ (5 %wt, pH = 8.0), while Oxone® was slowly added; t = 25-50 min. b Determined with GC. c *Cis/trans* epoxide ratio d Determined with chiral GC. e Optical configuration: 2R,3R (*cis*-epoxide). f Optical configuration: 2S,3R (*trans*-epoxide). g Optical configuration: R. h Optical configuration: 1S, 2R. i The optical configuration was assigned by comparison with those reported in the literature [34, 38].

were obtained for the unfunctionalized olefins. In all cases high selectivities found for the homogeneous catalyst were obtained for the heterogeneous systems, too. Additionally, the *cis/trans*-epoxide ratio for the *cis*-ethylcinnamate epoxidation was almost unchanged. These results indicated that diffusion limitations, side reactions catalyzed by the support and immobilized complexes in the external surface did not influence the catalytic behaviour of Jacobsen's catalyst immobilized into the mesopores of Al-MCM-41. Over MCM1HC and MCM2HC the highest enantioselectivities were obtained as in the homogeneous phase. However, the Mn content determined with ICP-AES showed a moderate leaching (between 10 and 30%), which indicates that the reaction could mainly be catalyzed in homogeneous phase. This fact can be anticipated due to the very weak interaction between catalyst and support.

On the other hand, MCM3HC proved to be very stable against leaching. However, enantioselectivities tremendously dropped. The reduced mobility of the immobilized complex inside the MCM3HC sample perhaps influences the catalytic performance negatively by inhibiting the appropriate geometric conformation needed for the chiral induction.
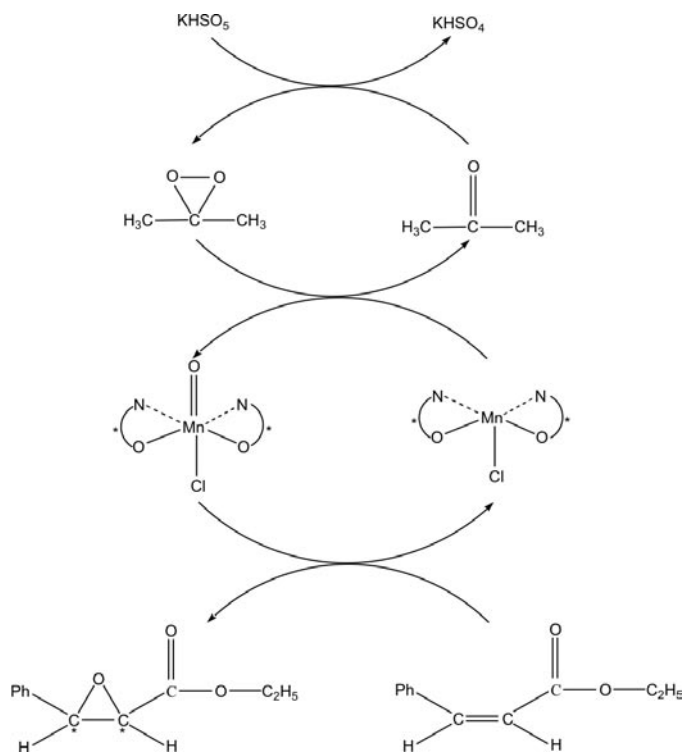
Figure 8 Proposed catalytic cycle for the enantioselective epoxidation of olefins using Mn (III)-salen complexes and *in situ* generated DMD as oxidizing agent
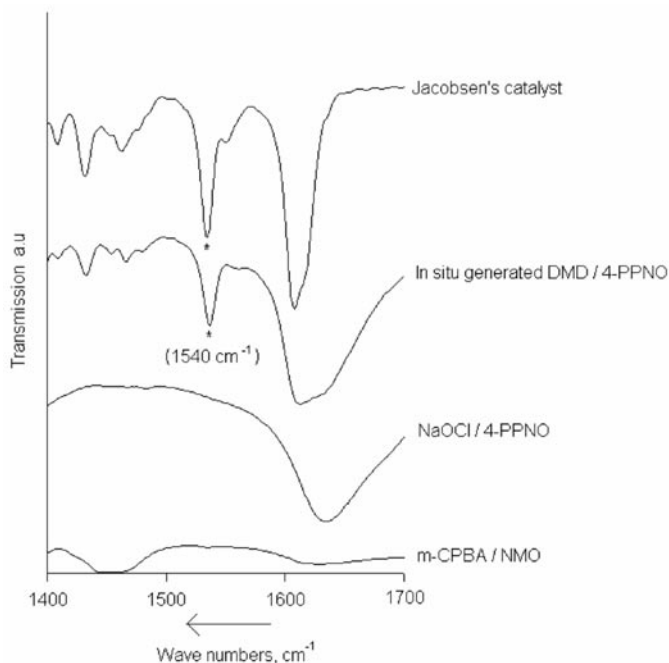

Figure 9 FTIR spectra of the Jacobsen's catalyst and MCM1HC used once in the epoxidation of 1,2-dihydronaphthalene with different oxidants

A possible reaction mechanism, in which DMD is formed from $KHSO_5$ and acetone during the reaction, is presented in figure 8. This catalytic cycle is based on the classical reaction mechanism which involves the direct use of the oxygen source with organometallic complex [39]. On the other hand, the use of O_2/aldehyde as oxidation system involves the *in situ* formation of several peroxyacid species, which react with the manganese salen complex to the catalytic active species [40]. Other examples of *in situ* generated oxidizing agents were found by Pietikäinen [41]. However, in these cases the formation of the active oxidant cannot be easily controlled by the use of a suitable chemical or physical properties, therefore the prolonged oxidation conditions cannot be suppressed.

Un-immobilized Jacobsen's catalyst could be recovered partially (80%, determined from Mn content by ICP-AES) in the *cis*-ethylcinnamate epoxidation by precipitation of the catalyst during the reaction [42]. It could be shown that the catalyst retained its selectivity and asymmetric induction as found for the fresh catalyst. However, some loss of conversion was found, which might be due to an incomplete catalyst recovery. These results demonstrate that the catalyst deactivation by oxidative

degradation of the salen ligand could be avoided when in situ generated DMD as oxidizing agent was used.

Figure 9 clearly shows that the band associated to the catalyst (located c.a $1540 \, cm^{-1}$) is only presented when *in situ* generated DMD as oxidizing agent was used. Therefore, the immobilized catalyst did not suffer any change in its structure, when *in situ* generated DMD was used as oxidizing agent. While the use of common oxidants such as NaOCl and *m*-CPBA destroyed the catalyst upon reaction. Additionally, the degradation of the salen ligand was strongly influenced by the substrate reactivity. Thus, using olefins which are easier to oxidize, the degradation of the catalyst can be prevented by stopping the reaction prior to complete conversion.

Finally, the recyclability of the catalyst MCM3HC was investigated (see figures 10 and 11). Both the conversion and enantiomeric excesses could be maintained for at least three cycles. Using this catalyst, the ligand salen deactivation could be suppressed. Thus, MCM3HC is stable to the leaching by using covalent attachment on the salen ligand, and degradation of the salen ligand is reduced by using *in situ* generated DMD as oxidizing agent.
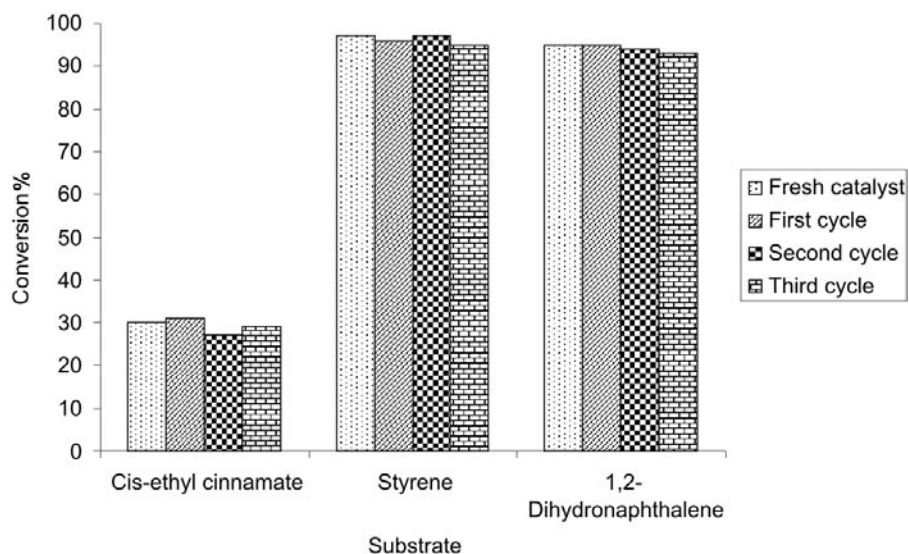

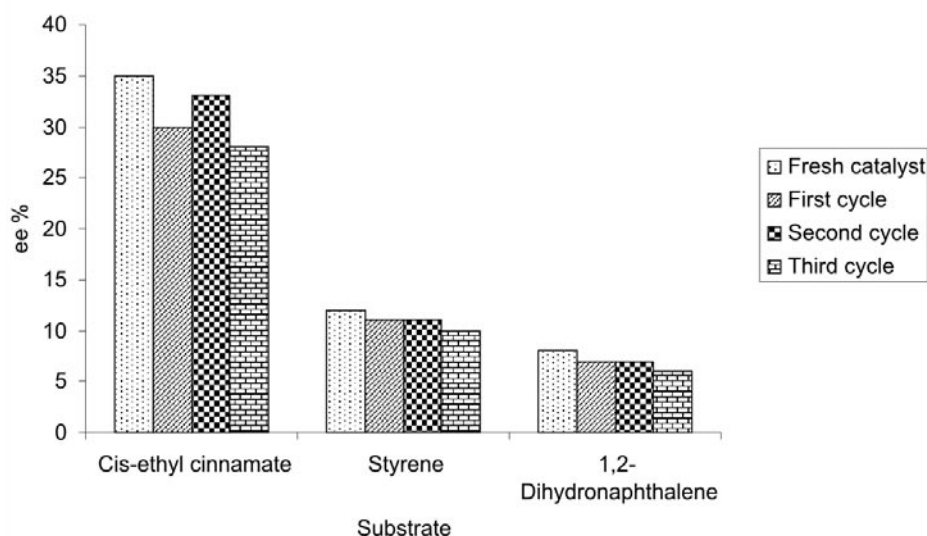**Figure 10** Effect of MCM3HC reuse on conversion

Figure 11 Effect of MCM3HC reuse on enantioselectivity

Conclusions

The methods of immobilization by no covalent attachment of the salen ligand (method 1, and method 2) showed a moderate leaching, although the same enantioselectivities as in homogeneous phase was reached. The stability towards leaching could be improved by covalent attachment of the catalyst on the modified surface of the Si-MCM-41 (method 3). However, the enantioselectivity was tremendously reduced probably to the low catalyst mobility, which produces a poor chiral communication with the substrate. The asymmetric epoxidation of prochiral olefins was performed using the Jacobsen's catalyst and *in situ* generated DMD as oxidizing agent. Heterogeneous systems, based on Al-MCM-41 and NH_2-Si-MCM-41 as support have been proven to be very stable to the oxidative degradation of the salen ligand.

Acknowledgements

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