Asymmetric epoxidation of styrene on the heterogenized chiral salen complexes prepared from organo-functionalized mesoporous materials

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Organosilane-modified mesoporous materials have been prepared under mild and acidic conditions by a solvent evaporation method using C_{16}TMABr surfactant as a template. The mesoporous samples synthesized in ethanol solvent by using this evaporation method showed a fully disordered pore system, but those obtained under hydrothermal conditions had highly ordered pores. The chiral salen Mn(III) complexes were immobilized on these organosilane-functionalized mesoporous silicas by a grafting method. The catalysts used in the asymmetric epoxidation of styrene and *cis*-stilbene and the effect of different mesoporous structures on the reactivity was investigated. Similar enantioselectivities were observed by using these heterogenized salen complexes as compared with reaction under homogeneous conditions.

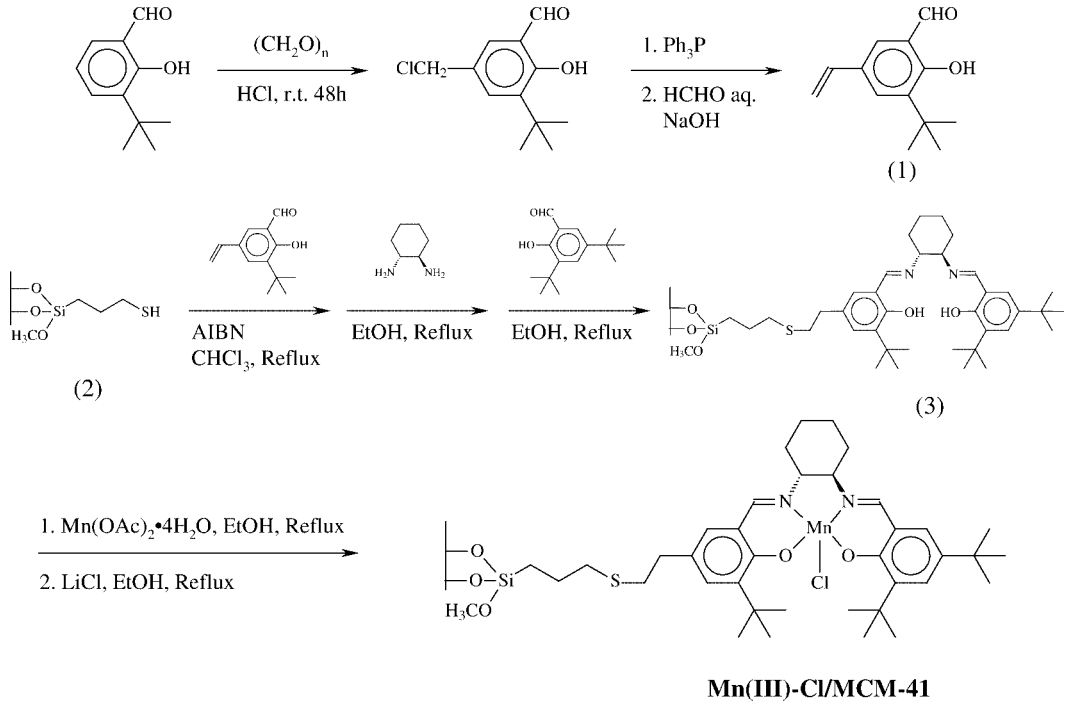
KEY WORDS: mercaptopropyltrimethoxysilane; MCM-41; salen; epoxidation; immobilization

1. Introduction

One of the M41S family shows a hexagonal array of uniform mesopores which depends on the type of template and synthesis conditions employed [1,2]. MCM-41 can be prepared hydrothermally and the formation of it from sodium silicate and hexadecyltrimethylammonium chloride in aqueous solution is known to be very sensitive to pH [3]. Neutralization of the produced NaOH with acetic acid to pH *ca.* 11 shifts the reaction equilibrium toward the formation of MCM-41. This synthesis method using repeated addition of acetic acid gives much higher quality of MCM-41 than procedures using pH adjustment at the beginning of reaction [3]. Recently, Roh *et al.* [4] have synthesized mesoporous silica in acidic conditions by a solvent evaporation method which accelerates supramolecular interactions involving condensation of cationic inorganic species in the presence of similarly charged surfactant molecules. This solvent evaporation synthesis has the advantages of very short reaction time and mild reaction condition. As a result, hexagonal arrayed mesoporous materials could be successfully synthesized within a few hours. Our investigations on the synthesis of mesoporous materials by this solvent evaporation showed that the pore size and pore structure could be controlled by the addition of trimethylbenzene and methanol (or ethanol) [5]. The mesoporous silicas prepared in the ethanol solvent exhibited a fully disordered channel structure. But the regular pore structure was obtained when methanol was used as a solvent. The mesoporous silicas having a wormhole framework are generally known to be more active than those having the ordered hexagonal pores in heterogeneous catalysis. This enhanced reactivity may result from a pore network connected in three dimensions, allowing easier access of reactants to active sites. Guth and co-workers [6] have reported the synthesis of disordered mesoporous silicas using a sodium silicate in the presence of Triton-X 100. Recently, Kim *et al.* [7] have prepared thermally stable mesoporous silicas having a wormhole framework structure from soluble silicate precursors.

Chiral (salen) Mn(III) complexes have been found to be highly enantioselective for the asymmetric epoxidation of conjugated *cis*-disubstituted and trisubstituted olefins [8–13]. The increasing interest towards this reaction led some authors to develop heterogeneous chiral Mn(III) salen catalysts. As introduced by some authors, the reported papers dealt with the immobilization method of chiral salen ligands by the condensation of functional groups. The anchoring method of reacting a functionalized ligand with reactive groups of organic and inorganic compounds (MCM-41), step by step, makes it possible to synthesize various unsymmetrical chiral salens of different structure and to immobilize them onto inorganic supports [14]. Frunza *et al.* [15] have investigated the embedding of enantioselective homogeneous chiral Mn(III) cationic salen complexes onto mesoporous MCM-41 materials.

Surface reactions exploiting terminal silanol groups have long been performed with amorphous supports or crystalline materials for application in catalysis. In utilizing the chemical reactivity of the mesoporous host, a number of functional groups have been covalently anchored to the channel walls, including ligands intended for the attachment of metal complexes. The introduction of functional organic groups has been performed through attachment of silane-



Scheme 1.

coupling agents to the mesoporous walls of previously synthesized and calcined MCM materials. The functional group is either directly incorporated in a silane-coupling agent or grafted onto it in a second or further reaction step. However, since the synthesis of mesoporous materials is a template-assisted sol–gel process, it has been recognized that the co-condensation of siloxanes and organosiloxane precursors during MCM formation can result in new hybrid materials [16,17]. The co-condensation route was pioneered by Sierra *et al.* [6] who documented the possibility of reacting the silica precursor TEOS with various silanes in the presence of surfactant template to result in the hybrid mesoporous MCM-41 materials. In the original synthesis of MCM-41, removal of the surfactant template was typically performed through calcinations at 550 °C. However, the hybrid mesoporous materials containing organosilane require extraction of the template at low temperature and these materials are known to be stable upon extraction in alcoholic HCl solution.

Here we demonstrate the synthesis of the heterogenized chiral salen catalyst on the 3-mercaptopropyltrimethoxysilane-modified MCM-41 by grafting. This grafting gives the advantage that it is possible to synthesize the various chiral salens of different structure. We report herein that organo-functionalized mesoporous materials could be synthesized by the solvent evaporation method and this mesoporous material was used to immobilize the chiral salen complexes on it. In addition, the effect of different mesoporous structures on the reactivity was investigated for the enantioselective epoxidation of styrene ansd *cis*-stilbene.

2. Experimental

For this study, the chiral salen complexes were synthesized and immobilized onto the MCM-41 by a multi-grafting method according to the procedure as shown in scheme 1.

The effect of different mesoporous structures on the reactivity was investigated for the enantioselective epoxidation of olefins. For this purpose, the mesoporous materials having fully ordered hexagonal pores or disordered wormhole structures were synthesized by a fast solvent evaporation method, and an organo-silane such as mercaptopropyltrimethoxysilane (MPTS) was added to the reactant mixture during the synthesis to obtain the organo-functionalized mesoporous silicas. In addition, the homogeneous chiral salen complexes were synthesized to evaluate and to compare the enantioselectivity in the asymmetric epoxidation reaction.

2.1. Preparation of MCM-41

An organosilane-functionalized mesoporous silica was synthesized according to the procedure as follows: tetraethylorthosilicate (TEOS; 50 g) and ethanol (33 g) were added to the pure water (35 g) and this mixture was heated to reflux for 10 min. HCl (1.25 g) was added dropwise and the mixture was vigorously stirred for 90 min. The mole ratio of TEOS : EtOH (or MeOH) : H_2O : HCl was $1 : 3 : 8 : 5 \times 10^{-2}$. At first step, MPTS was added to the substrate mixture to obtain the organo-functionalized mesoporous materials and hydrolysis reaction was performed. The amount of MPTS added was controlled and the mole ratio of MPTS/TEOS

was varied (0.05–0.25)/1.0. The reactant mixture was cooled to 25 °C and then stirred again for 30 min. The sample was aged at 50 °C for 30 min without agitation. The mixture was diluted with 360 g ethanol (or equivalent MeOH), and *n*-hexadecyl trimethylammonium bromide (C_{16}TMABr; 8.75 g, Aldrich Co.) was dissolved in the resulting solution. After stirring for 30 min, the solvent was evaporated at 60 °C. The surfactants were removed by repeated extraction using 1.5 wt% HCl/MeOH solution. The synthesized MCM-41 samples were characterized by XRD analysis.

2.2. Preparation of chiral (salen) Mn(III) complexes immobilized on MCM-41

The 3-*tert*-butyl-5-chloromethyl-2-hydroxybenzaldehyde was synthesized from 3-*tert*-butyl-2-hydrohybenzaldehyde by chloromethylation. 13.4 g (0.075 mol) of 3-*tert*-butyl-2-hydrohybenzaldehyde was treated with 5.0 g of paraformaldehyde in 50 ml of conc. HCl. After stirring for 48 h at room temperature, the reaction mixture was repeatedly extracted with diethyl ether. The organic phases were washed with saturated aqueous $NaHCO_3$ and brine and then dried over $MgSO_4$. The viscous oil was obtained by evaporation of the solvent. This product (15.9 g, 0.07 mol) was dissolved in benzene (150 ml). To a solution of benzylchloride in benzene was added 18.3 g of triphenylphosphine, and the mixture was heated under reflux for 1 h. After cooling down the solution at room temperature, the product was filtered off, washed with diethyl ether and dried under vacuum, giving 30.9 g of product salt as a white powder. To a vigorously stirred suspension of the phosphonium salt (24.6 g, 0.05 mol) in 170 ml of 37% aqueous formaldehyde was dropwise added a solution of 1.5 M NaOH (55 ml), keeping the reaction temperature below 40 °C. After 2 h at room temperature, the alkaline mixture was cooled in ice and neutralized with 6 N HCl. At pH = 7, the aqueous phase was extracted with benzene. Evaporation of the solvent afforded a semisolid which was firstly purified by flash chromatography (petroleum ether : acetone = 2 : 1) and then distilled under vacuum. The light yellow crystal of 3-*tert*-butyl-2-hydroxy-5-vinylbenzaldehyde (**1**) was obtained in 57% yield. To immobilize the salen ligand, mercaptopropylsilyl-functionalized mesoporous material (**2**) was used. 5 g of mercaptopropylsilyl-functionalized MCM-41, 200 mg (1.22 mmol) of AIBN and 1 g (4.85 mmol) of 3-*tert*-butyl-2-hydroxy-5-vinylbenzaldehyde were mixed together under nitrogen in oxygen-free 20 ml $CHCl_3$. The mixture solution was heated to 80 °C for 12 h. After finishing reaction and cooling, the sample was collected by filtration, washing with ether and methanol. The sample was dried in vacuum at 40 °C for 2 h. The heterogenized salen ligand (**3**) was prepared by the sequent reaction of the chiral half-unit immobilized on the solid support with corresponding excess (1R,2R)-(−)-1,2-diaminocyclohexane and salicylaldehyde derivatives (salicylaldehyde or 2,4-di-*tert*-butyl-salicylaldehyde) in a refluxing ethanol for 12 h.

The number of thiol sites on MCM-41 was determined by the weight loss in the temperature range between 300 and 700 °C with thermogravimetry (TG). The extent of reaction to make a Schiff base linkage was also determined by TG in every step of its synthesis. TGA was performed on a DuPont 951 thermogravimetric analyzer.

The chiral salen Mn(II) complexes immobilized on MCM-41 were readily accomplished by refluxing an ethanolic solution of a salen ligand (10) with 2 equiv. of Mn(II) acetate tetrahydrate in air for 2 h. Then, 3.0 equiv. of LiCl was added and the mixture was heated to reflux for an additional 1.0 h to obtain the Mn(III) salen complexes, as shown in scheme 1. The resulting dark brown powder Mn(III)–Cl/MCM-41 was filtered and washed several times with methylene chloride and methanol.

2.3. Preparation of the homogeneous salen complex

The symmetrical chiral salen ligand was easily obtained in about 90% yield by the reaction of 10 mmol 2,4-di-*tert*-butylsalicylaldehyde with 20 mmol (1S,2S)-(+)-1,2-diaminocyclohexane in a boiling ethanol solution. Mn(III) type complexes could be obtained by the treatment, as mentioned above. This catalyst will be denoted as Mn(III)–Cl.

2.4. The characterization of catalyst and asymmetric epoxidation reaction

The synthesized mesoporous materials were characterized by TEM and XRD. The characterization of the chiral salen complexes immobilized on MCM-41 was carried out using UV-vis reflectance spectroscopy. The general procedure for the asymmetric epoxidation follows the method as shown in the reported papers [8,9]. The ee% values were determined by capillary GC using chiral columns (CHORALDEXTM, Gamma-cyclodextrin trifluoroacetyl, 40 m × 0.25 mm i.d. (Astec)) and by vibrational circular dichroism spectroscopy (Chiral ir, Bomem).

3. Results and discussion

All the samples were characterized by XRD after synthesis. Organosilane-functionalized mesoporous materials were first synthesized by the solvent evaporation method to immobilize the chiral salen ligans on the surfaces. Figure 1 shows the X-ray diffraction patterns of mesoporous silicas obtained in an acidic condition using a C_{16}TMABr template. A series of samples were obtained with increasing organosilane content. The obtained mesoporous material showed a very intense (100) peak in the X-ray powder diffractogram when no MPTS was added into the substrate. This (100) diffraction peak decreased with increasing amount of MPTS (MPTS/TEOS ratio up to 0.25). Furthermore, when the solvent evaporation method using ethanol solvent was adopted to synthesize mesoporous silicas, the X-ray diffraction pattern showed a very weak and broad intensity for (110) and (200) reflections. The samples obtained

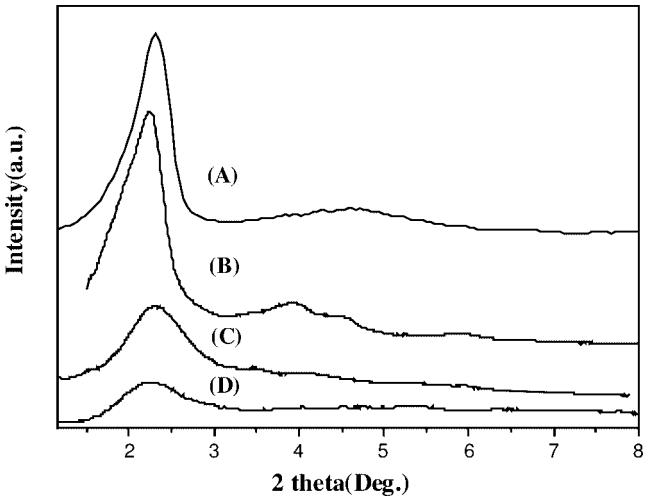


Figure 1. XRD patterns of samples obtained with different MPTS/TEOS ratios in ethanol (A) and methanol (B)–(D) solvents. MPTS/TEOS ratios: 0.05 (A) and (B), 0.1 (C) and 0.25 (D).

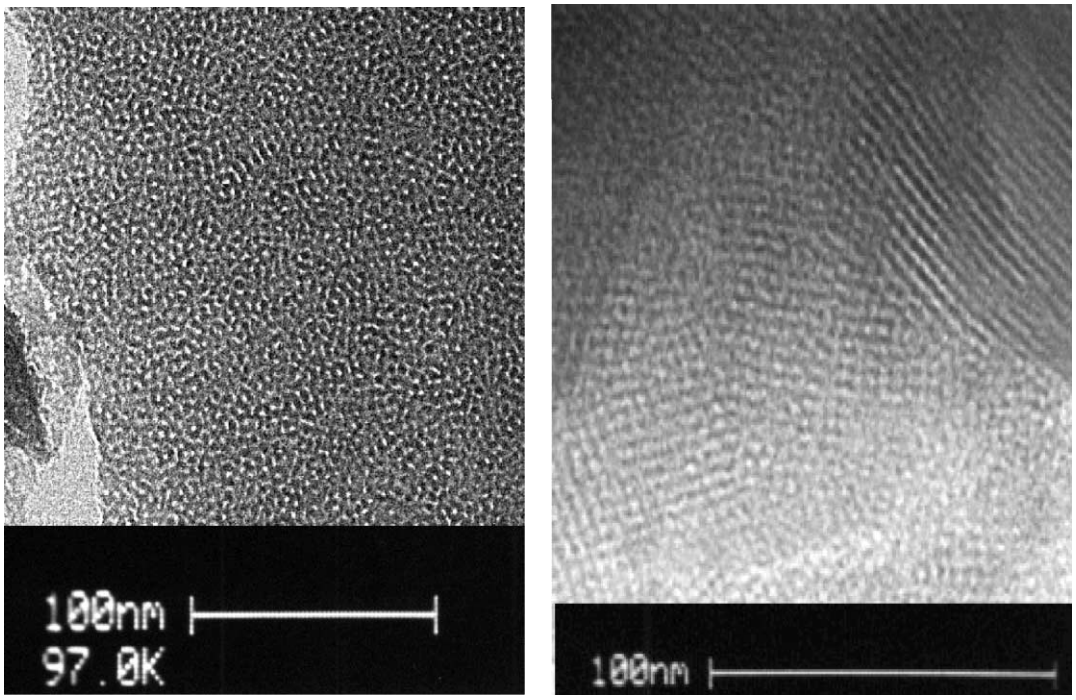
using methanol solvent exhibited XRD patterns with a very strong (100) diffraction peak with three weak but well resolved (110), (200) and (210) peaks. These four peaks are attributable to the hexagonal structure of obtained mesoporous silica. MCM-41 obtained by the solvent evaporation method was rigid and exhibited such high hardness that this sample could be reused over five times without any structural destruction in the epoxidation reaction.

In particular, the mesoporous materials showing the highest peak intensities in XRD patterns (sample (A) and (B) in figure 1) were used as a support to immobilize the chiral salens by following the procedure shown in scheme 1. The number of thiol groups calculated from TGA data is about 4.8 mmol/g-SiO_2. The compound **3** was obtained in 73–75 mol% yield on the basis of the mole number of compound **2**. This yield indicates that 3.5 mmol of salen ligand was immobilized on 1 g of MCM-41.

Figure 2 shows the TEM images of the organo-functionalized MCM-41 materials. The MCM-41 prepared in the acidic ethanol solvent by an evaporation method exhibited a fully disordered wormhole structure. This sample shows the branched network of pores similar to KIT-1 synthesized by Ryoo *et al.* in the alkaline media (pH = 10.2) using ethylenediaminetetraacetic acid tetrasodium salt [18]. The fully ordered pore system was investigated for MCM-41 samples synthesized by using methanol solvent under the same conditions.

In addition, as shown in figure 3, the networks of pore channel were examined using TEM after impregnation of Pt salt solution into the pores of ordered and disordered mesoporous materials, respectively, and followed reduction of Pt and HF dissolution of silica walls. The TEM photograph of figure 3(a) shows that the fully disordered wormhole-type material has a pore network that is connected in three dimensions. The short Pt-fibers were investigated for the samples having fully ordered mesopores as in figure 3(b), indicating that the mesoporous materials synthesized in methanol have disconnected one-dimensional pore system.

The diffuse reflectance UV-visible spectra shown in figure 4 are typical of chiral salen Mn(III) complexes. The chiral salen ligands of Mn(III) form showed the broad bands at near 250, 320, 420 and 500 nm on the UV spectra. But the Mn(II) acetate solution itself and Mn(II) acetate treated with



(a) (b)

Figure 2. TEM images of MCM-41s obtained by using ethanol (a) and methanol (b) solvents (MPTS/TEOS ratio 0.05).

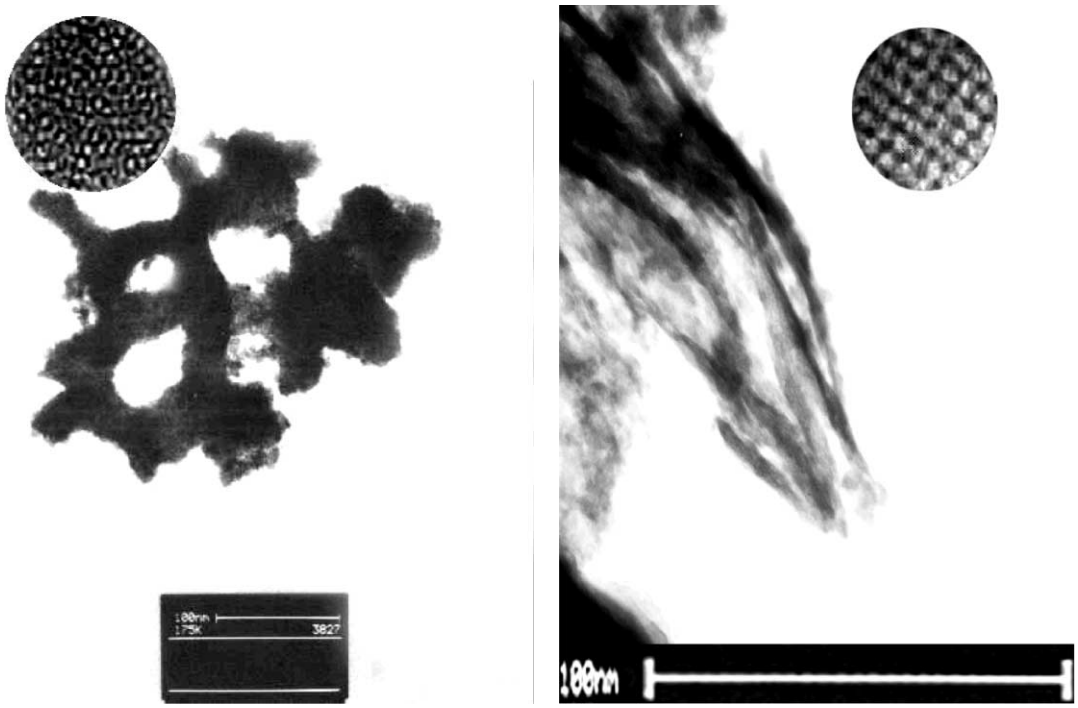


Figure 3. The TEM images of Pt-agglomerates impregnated in the pores of mesoporous silicas. Pt was reduced in hydrogen at 500 °C and the wall of mesoporous silica was dissolved in HF solution. MCM-41s were obtained using ethanol (a) and methanol (b) solvents.

LiCl in a refluxed methanol solution showed no absorption peak at above 300 nm. The broad bands at 420 and 500 nm are probably due to charge-transfer transitions in the Mn ions and charge-transfer transitions between the metal and ligand, respectively [14]. The characterization of the samples was also carried out using FTIR spectroscopy after immobilizing the salen complexes onto MCM-41. The characterization of the samples was also carried out using FTIR spectroscopy after synthesizing the Mn salen complexes and immobilizing them onto the MCM-41. In the IR spectra, all the salen complexes as well as MCM-41 loaded chiral salen ligand exhibited the characteristic imine band at 1630 cm^{-1}. This peak is assigned to the stretching vibration of the C–N bond. These results indicate that the successful anchoring of chiral salen ligands onto the MCM-41 surfaces was achieved.

The enantioselective catalytic activities of the (salen) Mn(III) chloride complex immobilized on MCM-41 and the homogeneous complex of same structure in solution were examined for the epoxidation of styrene and *cis*-stilbene, and the result of reaction is summarized in table 1. The enantiosectivity was found to increase significantly at the low temperature. As shown in table 1, a relatively high ee% value was obtained particularly by using NaOCl as an oxidant. For effects of oxidants, a mild oxidant NaOCl acts as a better

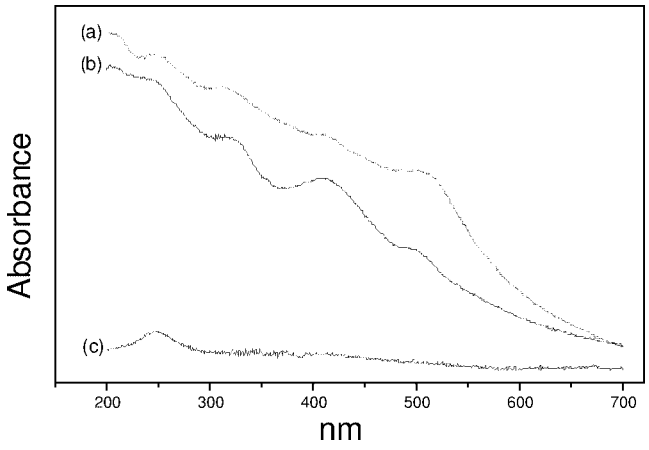


Figure 4. The diffuse reflectance UV-vis spectra of the homogeneous Mn(III) salen complex (a), the heterogenized Mn(III) salen complex on MCM-41 (b) and Mn(II)-ion-exchanged MCM-41 (c).

Table 1
The enantioselective epoxidation of olefins using various oxidants and catalysts

Substrate	Catalyst	Oxidant	Conv. (%)	ee% of epoxide	3rd recycle ee% (conv.)
Styrene	Mn(III)-B	*m*-CPBA[a]	97	46	
cis-Stilbene			98	35	
Styrene	Mn(III)-E		75	47	46(71)
cis-Stilbene	/MCM-41 (disordered)		66	36	36(63)
Styrene	Mn(III)-B	NaOCl[b]	97	48	
cis-Stilbene			98	43	
Styrene	Mn(III)-E		71	51	54(67)
cis-Stilbene	/MCM-41 (ordered)		63	43	42(61)

[a] Substrate : catalyst : *m*-CPBA : NMO = 1 : 0.05 : 2 : 5, reaction temp. = 0 °C, time = 30 min.

[b] Substrate : catalyst : NaOCl = 1 : 0.05 : 1.5 (pH = 11.3), reaction temp. = 0 °C, time = 4 h.

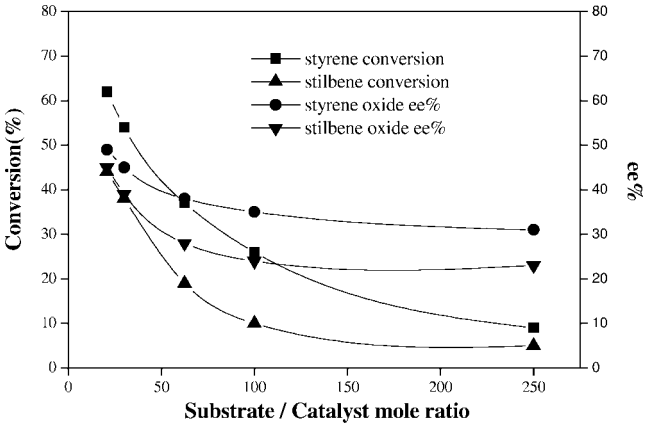


Figure 5. Conversions and ee% of products obtained in the asymmetric epoxidation of styrene and *cis*-stilbene. Catalyst Mn(III)–Cl/MCM-41 having hexagonally ordered pore channel, oxidant NaOCl.

oxidant than *m*-CPBA in enantiomeric excess of epoxides. But the use of NaOCl gave a disadvantage in reaction rates. This result is also shown in table 1. In particular, homogeneous chiral Mn(salen) complexes and heterogenized chiral salen Mn samples gave almost the same selectivity in the reaction. The immobilized chiral Mn salen/MCM-41 catalyst was also efficient in the epoxidation of *cis*-stilbene. It has been known that the chiral salen Mn(III) complexes show low selectivity for the epoxidation of *trans*-olefins. When the salen-immobilized MCM-41 was used as a catalyst, the pore structure of the mesoporous support had an effect on the catalytic activity for the asymmetric epoxidation. The conversions of styrene and *cis*-stilbene to epoxide were found to increase over the MCM-41 support having a disordered pore system as compared with that having hexagonally ordered channels. It is believed that the disordered pore system of MCM-41 synthesized by the solvent evaporation method has the advantage of the three-dimensional diffusion.

The enantioselective epoxidations of styrene and *cis*-stilbene were investigated using the immobilized chiral salen catalyst of Mn(III) at different substrate/catalyst mole ratios and the results are summarized in figures 5 and 6. The conversion of olefin and the ee% of epoxide increased as the substrate/catalyst ratio decreased. The racemic product was obtained only when the reaction was performed without addition of salen catalyst. This result indicates that the catalysed reaction over chiral complexes is competing with the achiral reaction as reported by Janssen *et al.* [19]. The effect of pore structures on the catalytic activity for the asymmetric epoxidation can be also investigated in these results. As can be seen in the results of figures 5 and 6, higher conversions were obtained with the salen complexes immobilized on the mesoporous silica having fully disordered type pores at the same reaction time and conditions. Even though a higher turnover number could be obtained over the salen catalyst immobilized on the wormhole type mesopores, the enantioselectivity (ee%) was not dependent on the type of pore structures in this reaction. The high asymmetry-inducing ability of the salen complex is attributed to the intense interaction of the substituent of salen ligands only near the metal center with incoming substrate.

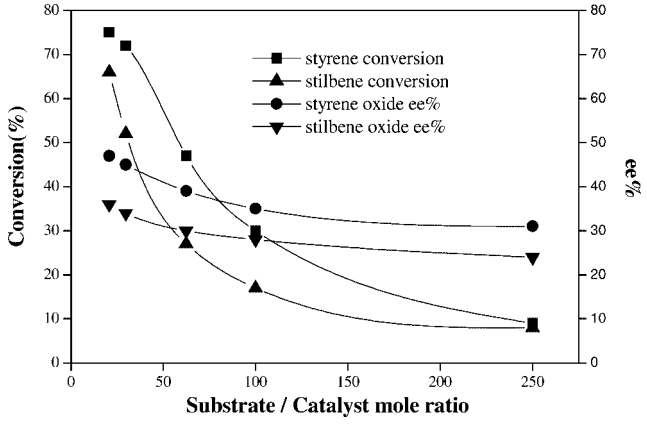


Figure 6. Conversions and ee% of products obtained in the asymmetric epoxidation of styrene and *cis*-stilbene. Catalyst Mn(III)–Cl/MCM-41 having fully disordered pore channel, oxidant NaOCl.

The *trans*- and *cis*-stilbene oxide were obtained simultaneously as products after the epoxidation reaction of *cis*-stilbene. The peaks for *trans*- and *cis*-stilbene oxide were found at different positions on the H-NMR spectra. The H-NMR spectrum of the reaction product was compared with that of pure *cis*- and *trans*-stilbene oxide as references and the ratio of *cis*-stilbene oxide/*trans*-stilbene oxide in the products could be calculated by H-NMR spectra. The *cis/trans* ratio of the product obtained on the heterogenized chiral salen catalyst was about 3, which was very similar to that observed for the equivalent homogeneous reactions. This ratio was not affected by changing the oxidant source. When *m*-CPBA/NMO was used as an oxidant, the *cis/trans* ratio of the product was 2.5. This effect suggests that the wall of the mesoporous silica support gave no steric hindrance on the transformation of *cis* to *trans*.

After using Mn(salen) complexes immobilized on MCM-41 as catalysts, the resultant solution exhibited no color and any presence of Mn was not detected in the solution. This means that Mn(III) salen complexes immobilized on mesoporous materials are stable during the reaction and exist in the pore system without any extraction. The catalytic activity and selectivity of immobilized Mn(salen) complexes have not changed more or less after four times of reusing. The catalyst could be reused after washing with CH_2Cl_2 solvent and drying under vacuum at 60 °C.

Vibrational circular dichroism (VCD) spectroscopy can be used to elucidate the stereochemistries of chiral molecules, including the accurate estimation of enantiomeric excess and their absolute configurations [20]. Optically pure samples were used as references to confirm the absolute configuration of the products. Three VCD spectra are shown in figure 7: one is a spectrum of 53% ee *trans*-stilbene oxide obtained over (R,R)Mn(III) salen catalyst, another is that of 52% ee *trans*-stilbene oxide and the other is that of racemic stilbene oxide obtained using the racemic Mn(III) salen complex as a catalyst. The comparison between the values of ee% determined by VCD and those measured by LC are in

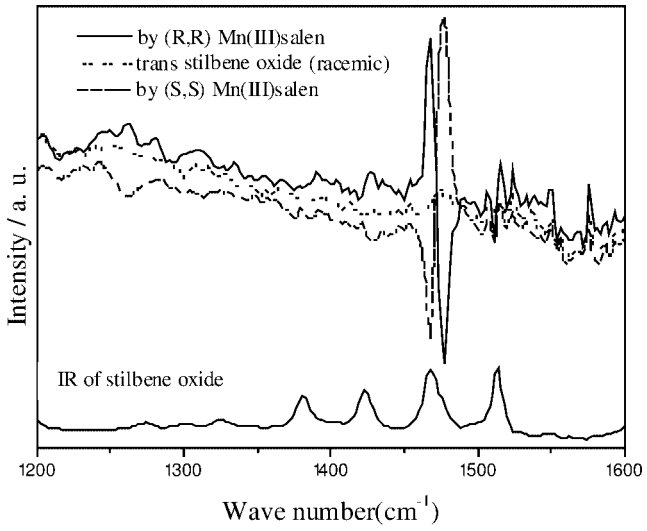


Figure 7. Vibrational circular dichroism (VCD) spectra of optical isomers obtained in the asymmetric epoxidation of *cis*-stilbene.

very good agreement to within 2% ee. The VCD spectra of opposite configuration, such as R,R(+) and S,S(−), exhibited the reverse absorbtion peaks as shown in figure 7. The FTIR spectrum is also shown in the same figure. These spectra have shown directly that the (S,S)-Mn(III) chiral salen complexes oxidized *cis*-stilbene to (S,S)-(−)-*trans*-epoxides in the asymmetric epoxidation. It is very helpful to determine the absolute configuration and ee% value by this VCD analysis for the asymmetric reactions.

4. Conclusions

The mercaptopropyltrimethoxysilane-modified mesoporous materials have been prepared by a solvent evaporation method using C_{16}TMABr surfactant as a template. The mesoporous samples synthesized in ethanol solvent showed a fully disordered pore system, but those obtained in methanol had highly ordered pores. The chiral Mn(III) salen complexes could be supported on the mesoporous MCM-41 through the condensation of the chiral half-unit immobilized on the solid support with corresponding excess 1,2-diaminocyclohexane and 2,4-di-*tert*-butylsalicylaldehyde in a refluxing ethanol. The asymmetric catalytic epoxidations of styrene and *cis*-stilbene using these catalysts have been applied with success. Higher conversions were obtained with the salen complexes immobilized on the mesoporous silica having fully disordered type pores at the same reaction time and conditions. On the basis of asymmetric epoxidation results, chiral salen complexes immobilized on a mesoporous material by the present procedure can be applied as an effective asymmetric catalyst of heterogeneous form.

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