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Synthesis of a Siliceous MCM-41 using C_{22}TMACl Template and Preparation of Heterogenized New Chiral Salen Complexes

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Abstract–Purely siliceous MCM-41 has been prepared under both mild and acidic conditions by a solvent evaporation method using C_{16}TMABr and C_{22}TMACl surfactant as templates. A hydrothermal synthesis was also carried out by utilizing a method of adjusting the gel pH to 10. The mesoporous samples synthesized in ethanol solvent by using this evaporation method showed a fully disordered pore system, but those obtained in the hydrothermal synthesis had highly ordered pores. The chiral salen Mn(III) complexes were immobilized on the siliceous MCM-41 by a new grafting method using 3-aminopropyltrimethylsilane and diformylphenols. These ligands on MCM-41 were stable during the reactions. High enantioselectivities were displayed in the epoxidation of styrene by using these heterogenized salen complexes.

Key words: Solvent Evaporation Method, MCM-41, Salen, Epoxidation, Immobilization

INTRODUCTION

One of the M41S family shows a hexagonal array of uniform mesopores which depends on the type of template and synthesis conditions employed. MCM-41 can be prepared hydrothermally by addition of 1,3,5-trimethylbenzene (TMB). The pore size of MCM-41 increased upto 10 nm with increasing amount of TMB. The formation of MCM-41 from sodium silicate and hexadecyltrimethylammonium chloride in aqueous solution is known to be very sensitive to pH [Ryoo and Kim, 1995]. Neutralization of the produced NaOH with acetic acid to pH ca. 11 shifts the reaction equilibrium toward the formation of MCM-41 [Ryoo and Kim, 1995]. The above 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. Namba et al. have succeeded in the hydrothermal synthesis of highly ordered siliceous MCM-41 using C_{22}TMACl as a template by reducing the pH (pH=9) at the beginning of reaction [Namba et al., 1998]. Moreover, the pore size of MCM-41 materials was finely controlled by using a template mixture of C_{16}TMABr/C_{22}TMACl. The pore size of the obtained MCM-41 was from 1.8 to 4.2 nm. Stucky et al. have reported that trilayer ($S^+X^-I^+$) hydrogen bonding is obtained by combining the cationic surfactant with cationic silica species at acidic pH values below the aqueous silica isoelectric point (SIP) [Stucky et al., 1997]. This pathway is mediated by counterion of opposite charge to that of the surfactant head groups. In the case of $S^+X^-I^+$ system, the mesoporous structure is formed at pH values below the SIP. Recently, Roh et al. have synthesized the mesoporous silica in acidic condition by solvent evaporation method which accelerates supramolecular interactions involving condensation of cationic inorganic species in the presence of similarly charged surfactant molecules [Roh et al., 1999]. 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.

Chiral (salen)Mn(III) complexes have been found to be highly enantioselective for the asymmetric epoxidation of conjugated cis-disubstituted and trisubstituted olefins [Irie et al., 1990; Jacobson et al., 1991; Palucki et al., 1994]. The increasing interest toward this reaction brought some authors to develop the heterogeneous chiral Mn(III) salen catalysts. However, to date, three kinds of approaches have been adopted: First, chiral Mn salen complexes were supported on polymers. As an application, Janssen et al. have synthesized a dimeric form of (salen)Mn(III) ligand and retained this complex in the crosslink polymer membrane to use as a catalyst for epoxidation [Janssen et al., 1997]. Minutolo et al. have synthesized polymer-bound chiral salen Mn(III) complex by copolymerization of salen complex with styrene and divinylbenzene [Minutolo et al., 1996]. They showed the catalyst could effectively be recovered and reused several times without loss of activity and stereoselectivity.

Second, the encapsulation of salen complex using the ship-in-bottle method was applied. Sabater et al. have synthesized a chiral (salen)Mn(III) complex of simple structure inside the supercage of zeolite Y, showing catalytic activity very similar to that of chloride complex in the homogeneous phase [Sabater et al., 1997]. Ogunwumi and Bein have reported that asymmetric (salen) Mn(III) complexes were assembled and trapped in the cages of zeolite EMT in a multistep synthesis and these heterogeneous catalyst produced a high enantiometric excess in the epoxidations of aromatic alkenes with NaOCl [Ogunwumi and Bein, 1997].

Third, Mn salen ligands were immobilized by ion exchange reaction. Piaggio et al. have reported that Mn-exchanged MCM-41 modified with a chiral salen was an effective catalyst for the

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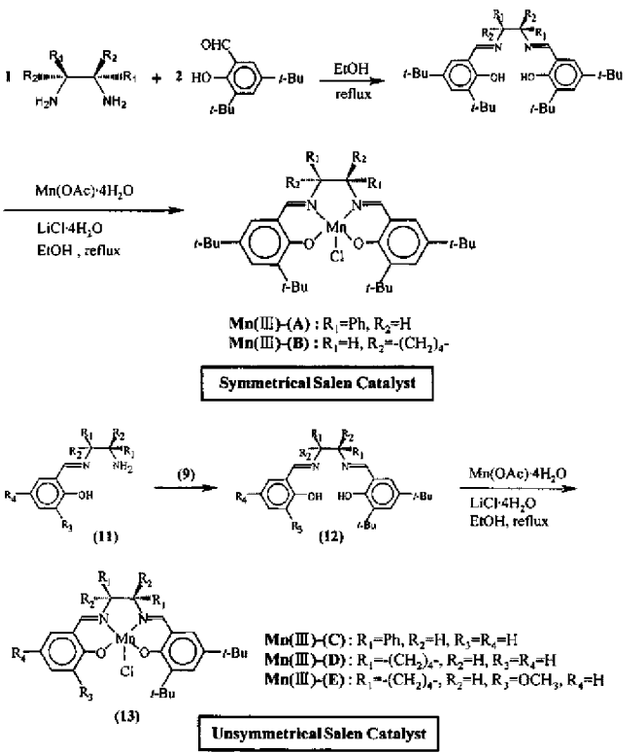
epoxidation of cis-stilbene [Piaggio et al., 1998]. We have also immobilized the cationic type of chiral Mn(III) salen complexes into the Al-MCM-41 by ion exchange [Kim and Kim, 1999]. Recently, Frunza et al. have investigated the embedding of enantioselective homogeneous chiral Mn(III) cationic salen complexes into the pore of mesoporous MCM-41 materials [Frunza et al., 1997]. Very few asymmetric catalytic reactions have been examined using chiral salen complexes immobilized on MCM-41. As introduced by some authors, the immobilized chiral salen has been obtained mainly by the condensation of unsaturated olefin groups in salen structure with styrene and divinylbenzene.

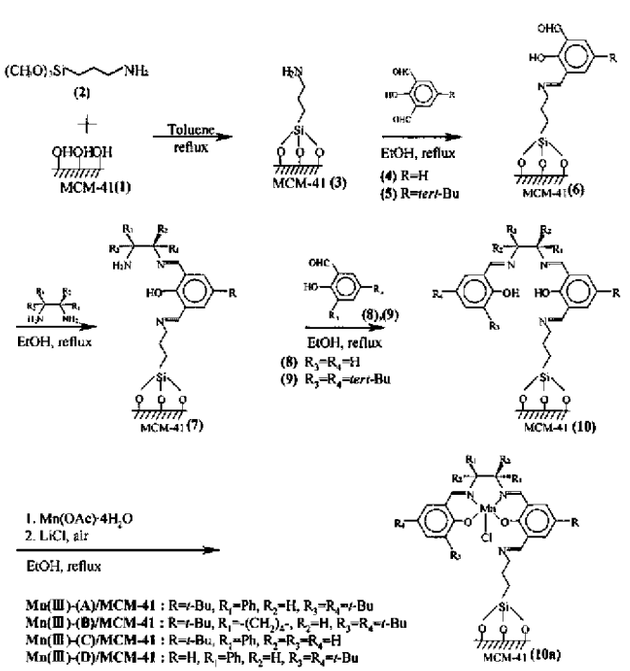
Here we demonstrate the synthesis of the heterogenized chiral salen catalyst on the siliceous MCM-41 by new grafting method using 3-aminopropyltrimethoxysilane and 2,6-diformyl-4-tert-butylphenol. This grafting method has the advantage that the ligand preferentially bind at locations on MCM-41 surface accessible for the substrate during a catalytic reaction. By this new grafting method using a diformylphenol as a building block of salen structure, it is possible to synthesize the various unsymmetrical chiral salens of different structure. We report herein that these new catalysts afford relatively high level of enantioselectivity in the asymmetric epoxidation of styrene. In addition, we synthesized a siliceous MCM-41 by solvent evaporation using C_{22}TMACl surfactant as a template, and this mesoporous material was used to immobilize the new chiral salen complexes on it by a multistep-anchoring method.



Scheme 2.

EXPERIMENTAL

For this study, the chiral salen complexes were synthesized and immobilized onto the MCM-41 by a new multi-grafting method according to the procedure as shown in Scheme 1. In addition, the homogeneous symmetrical and unsymmetrical chiral salen complexes were synthesized to evaluate and to compare the enantioselectivity in the asymmetric epoxidation reaction, respectively. The procedure for the synthesis of homogeneous complexes is also shown in Scheme 2.



Scheme 1.

1. Preparation of MCM-41

A purely siliceous MCM-41**(1)** was synthesized according to the following procedure as reported by Roh et al. [Roh et al., 1999]. The MCM-41 of very high crystallinity could be synthesized within about 4 h by this modified method. Tetraethylorthosilicate (TEOS; 50 g) and ethanol (33 g) was 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:H_2O:HCl was $1:3:8:5\times10^{-2}$. 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 pure ethanol (360 g) and *n*-docosyltrimethylammonium chloride (C_{22}TMACl; Arquad 22-80, Lion Co.; 8.747 g) or equivalent n-hexadecyltrimethylammonium bromide (C_{16}TMABr; Aldrich Co.) was dissolved in the resulting solution. After being stirred for 30 min, the solvent was evaporated at 60 °C. The resultant dried solid was heated to 550 °C at the heating rate of 1 °C/min and then calcined at 550 °C in air for 6 h. In addition, MCM-41 was also synthesized hydrothermally by using NaOH and Ludox HS 40 as a silica source. C_{16}TMABr and C_{22}TMACl were also used as a template, respectively, in this method. The reaction mixture was heated to 100 °C for 24 h and the pH was adjusted to 10 by dropwise addition of dilute H_2SO_4. The synthesized MCM-41 samples were characterized by XRD analysis and N_2 adsorption for determination of pore size distribution.

2. Preparation of Chiral (salen)Mn(III) complexes immobilized on MCM-41

A suspension of 5.38 g of 3-aminopropyltrimethoxysilane**(2)** and 20 g of MCM-41 in 100 mL of toluene was heated to reflux with stirring. After being heated for 3 h, 25 mL of solution containing methanol and toluene was distilled from the mixture. 25 mL of methanol-toluene solution was distilled out after an additional 1 h refluxing. The mixture was refluxed again for 30 min and cooled. The powder sample was filtered and washed with diethylether. The compound of 3-aminopropylsilyl-functionalised MCM-41 **(3)** was obtained in a 21.5 g yield. This yield indicates that 0.84 mmol of **(2)** was immobilized on 1 g of **(1)**.

2,6-Diformylphenol**(4)** was synthesized by a three-step procedure from 2,6-dimethylphenol with high yield and good reproducibility as reported by Zondervan et al. [Zondervan et al., 1997].

4-*Tert*-butyl-2,6-diformylphenol**(5)** was synthesized according to the procedure described by Chang et al. [Chang et al., 1988]. The compound **(6)** was prepared by the reaction of **(4)** or **(5)** with 2.2 equiv. of **(3)** in a refluxing ethanol solution for 10 h, respectively. After cooling, **(6)** was collected by filtration, washed with ether and methanol. The sample was dried in vacuum (2 mmHg) at 40 °C for 2 h. The chiral half-unit immobilized on MCM-41 **(7)** was obtained by the condensation of **(6)** and the available chiral auxiliary (1S,2S)-(+)-1,2-diphenylethylenediamine or (1S, 2S)-(+)-1,2-diaminocyclohexane with 2.2 equiv. in the boiling ethanol for 14 h. After cooling, **(7)** was collected by filtration, washed with methylenechloride and methanol, and dried in vacuum at 40 °C.

2,4-Di-*tert*-butyl salicylaldehyde**(9)** was synthesized by the reaction of 2,4-di-*tert*-butylphenol and paraformaldehyde in a refluxed anhydrous toluene according to the procedure reported in the literature [Casiraghi et al., 1980]. To the two-neck round-bottom flask equipped with a reflux condenser, mechanical stirrer and thermometer, anhydrous toluene (30 mL), 2,4-di-*tert*-butylphenol (3 g, 14.54 mmol), tin(IV)tetrachloride (378 mg, 1.45 mmol), and 2,6-lutidine (624 mg, 5.82 mmol) were added in a nitrogen environment. The mixture was stirred for 20 min at room temperature, and then the paraformaldehyde (961 mg, 32 mmol) was added. The resulting yellowish solution was heated at 100 °C for 8 h. After cooling, the reaction mixture was poured into the water, acidified to pH=2 with 2N-HCl, and extracted with diethylether. The ether extract was washed with a saturated NaCl solution, dried with $MgSO_4$, and concentrated to leave a crude salicyaldehyde. The product was purified by flash chromatography on silica gel (n-hexane:ethyl acetate =9.5:0.5, volume ratio). Complete removal of solvents from the resulting filtrates provided 2,4-di-*tert*-butyl salicylaldehyde. Salicyaldehyde**(8)** was obtained from Aldrich Co. and used without purification.

The compound **(10)** was prepared by the reaction of the chiral half-unit immobilized on MCM-41**(7)** with corresponding excess salicylaldehyde derivatives (salicylaldehyde**(8)** or 2,4-di-*tert*-butyl salicylaldehyde**(9)**) in a refluxing ethanol for 18 h. Then, the chiral salen Mn(II) complexes immobilized 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) complexes as shown in Scheme 1. The resulting dark brown powder **(10a)** was filtered and washed several times with methylene chloride and methanol.

3. Preparation of the Homogeneous Symmetrical and Unsymmetrical Salen Complexes

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 (or (1S,2S)-(−)-1,2-diphenyl ethylenediamine) in a boiling ethanol solution. Mn(III) type complexes could be obtained by the treatment as mentioned above (Scheme 2). For the synthesis of unsymmetrical salen complexes, 10 mmol salicylaldehyde in 50 ml chloroform was added dropwise to a stirred solution of 30 mmol (1S,2S)-(+)-1,2-diaminocyclohexane (or (1S,2S)-(−)-1,2-diphenylethylenediamine) in 100 ml chloroform containing molecular sieve 4A at 0 °C. The addition of salicylaldehyde took 5 h. A pale-yellow creamy solid**(11)**, namely chiral half-unit, was obtained after evaporation of solvent under vacuum and washing with water to remove the unreacted diamines [Lopez et al., 1998]. 10 mmol of the chiral half-unit**(11)** in 20 ml ethanol was added dropwise to corresponding salicylaldehyde derivative (10 mmol) in 20 ml of ethanol at room temperature. The mixture was heated to 60 °C and stirred for 8 h. The resulting yellow solid**(12)** was collected by filtration and recrystallized from ethanol. Then, the chiral salen Mn(II) complexes**(13)** were readily accomplished by refluxing ethanolic solutions of a salen ligand**(12)** with Mn(II) acetate tetrahydrate and LiCl, respectively (Scheme 2). In addition, the conventional symmetrical salen ligands were also synthesized according to the procedure described by Chang et al. as shown in Scheme 2 [Chang et al., 1988].

4. The Characterization of Catalyst and Asymmetric Epoxiation Reaction

The synthesized mesoporous materials were characterized by TEM and XRD. The pore size distribution was determined by N_2 adsorption at liquid nitrogen temperature (BJH method). The characterization of the chiral salen complexes immobilized on MCM-41 was carried out by using UV-vis reflectance spectroscopy.

The general procedure for the asymmetric epoxidation is as follows: A solution of 0.96 mmol olefin, 4.8 mmol *N*-methylmorpholine *N*-oxide (NMO), 0.038 mmol chiral salen Mn(III) complex in 10 ml of CH_2Cl_2 solution was cooled to −80 °C. The solid *m*-chloroperoxobenzoic acid (*m*-CPBA, 1.92 mmol) was added in four equal portions. The reaction mixture was stirred for 2 h at −80 °C and 10 ml of 1 N NaOH was added. The organic phase was washed with brine and dried over $MgSO_4$. The ee% values were determined by capillary GC using a chiral column (CHORALDEXTM, Gamma-cyclodextrin trifluoroacetyl, 40 m×0.25 mm i.d. (Astec)) and by vibrational Circular Dichroism spectroscopy (Chiral ir, Bomem).

RESULTS AND DISCUSSION

Fig. 1 shows the X-ray diffraction patterns of MCM-41s which were obtained by the solvent evaporation method in an acidic condition and the conventional hydrothermal synthesis using C_{16}TMABr and C_{22}TMACl template respectively. The obtained

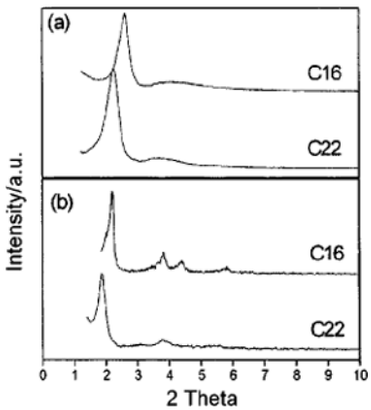


Fig. 1. X-RD patterns of MCM-41s obtained by the solvent evaporation method (a) and by the hydrothermal synthesis (b).
C16; C_{16}TMABr, C22; C_{22}TMACl surfactant

MCM-41 showed a very intense (100) peak in the X-ray powder diffractogram. This (100) diffraction peak shifted to the lower 2θ value by using C_{22}TMACl, instead of C_{16}TMABr, indicating a significant lattice expansion. The calculated d_{100}-spacing of calcined MCM-41 was 5.2 nm and 4.1 nm when the MCM-41 was synthesized by the conventional hydrothermal preparation. That was 4.7 nm and 3.7 nm for MCM-41 obtained by the solvent evaporation method. The BJH pore size distributions of the mesoporous materials are shown in Fig. 2. The pore size determined by N_2 adsorption was 4.3 nm for the sample synthesized by the hydrothermal method, and then that was 3.8 nm by the evaporation method when the added surfactant was same C_{22}TMACl. Furthermore, when the solvent evaporation method was adopted to synthesize MCM-41, the X-ray diffraction pattern showed a very weak and broad intensity for (110) and (200) reflections. The MCM-41 samples having different pore size and structures (4 samples as shown in Fig. 1 and 2) were used to immobilize the chiral salen complexes on it by following the procedure shown in Scheme 1. The XRD intensities of MCM-41

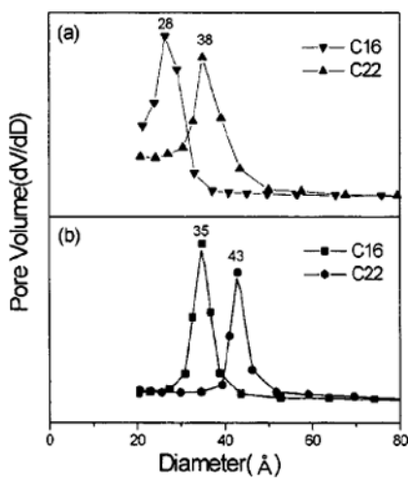


Fig. 2. The pore size distributions of MCM-41s obtained by the solvent evaporation method (a) and by the hydrothermal synthesis (b).

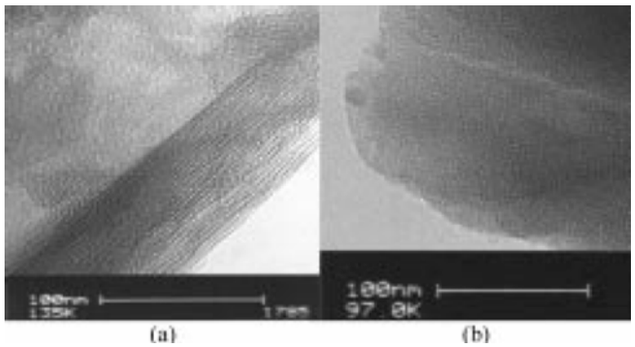


Fig. 3. TEM images of MCM-41s obtained by the hydrothermal synthesis (a) and by the solvent evaporation method (b).

have not changed after immobilization of chiral salen complexes. Furthermore, 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.

Fig. 3 shows the TEM images of purely siliceous MCM-41. These samples were obtained by using C_{22}TMACl surfactant as a template. The MCM-41 prepared in the acidic mixture by a solvent evaporation method exhibited a fully disordered channel 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 [Ryoo et al., 1997]. The fully ordered pore system was investigated for MCM-41 samples synthesized by the conventional hydrothermal method at pH 10.

The diffuse reflectance UV-visible spectra shown in Fig. 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 LiCl in a refluxed methanol solution showed no absorption peak at above 300 nm. The broad bands at 420 nm and 500 nm are probably due to charge-transfer transitions in the Mn ions and charge transfer transitions between the metal and ligand, respectively [Frunza et

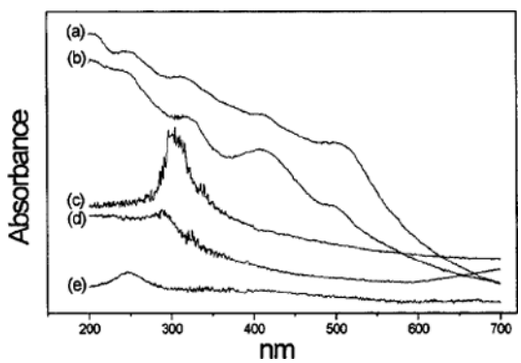
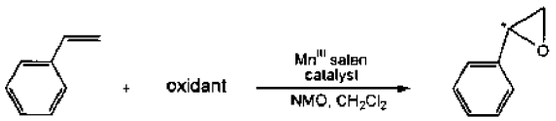


Fig. 4. The diffuse reflectance UV-vis spectra of the homogeneous Mn(III) salen complex (a), the heterogenized Mn(III) salen complex on MCM-41 (b), Mn(II) acetate solution (c), Mn(II) acetate treated with LiCl in a boiling methanol (d) and Mn(II) ion exchanged MCM-41 (e).

Table 1. Asymmetric epoxidation of olefins using homogeneous and heterogenized chiral Mn-salen complexes



Entry	Olefin	Catalyst[a]	Reaction temp. (K)	Conversion (%)	ee (%)
1	styrene	Mn(III)-A	195	98	43
2	styrene	Mn(III)-B	195	97	84
3	styrene	Mn(III)-C	195	88	54
4	styrene	Mn(III)-D	195	84	59
5	styrene	Mn(III)-E	273	98	66
6	styrene	Mn(III)-E	195	93	81
7	styrene	Mn(III)-A/MCM-41(H35)	195	62	85
8	styrene	Mn(III)-A/MCM-41(H43)	195	64	86
9	styrene	Mn(III)-A/MCM-41(S28)	195	73	86
10	styrene	Mn(III)-A/MCM-41(S38)	195	75	86
11	styrene	Mn(III)-B/MCM-41	195	73	65
12	styrene	Mn(III)-C/MCM-41	195	64	87
13	styrene	Mn(III)-D/MCM-41	195	67	73
14	α-methylstyrene	Mn(III)-A	195	97	66
15	α-methylstyrene	Mn(III)-B	195	90	43
16	α-methylstyrene	Mn(III)-A/MCM-41	195	74	56
17	α-methylstyrene	Mn(III)-B/MCM-41(H35)	195	54	71
18	α-methylstyrene	Mn(III)-B/MCM-41(H43)	195	58	70
19	α-methylstyrene	Mn(III)-B/MCM-41(S28)	195	68	71
20	α-methylstyrene	Mn(III)-B/MCM-41(S38)	195	70	72

[a]MCM-41 obtained by the hydrothermal synthesis is denoted as H and by the solvent evaporation method as S, respectively. The number in the parentheses means the mean pore size of MCM-41.
[b]Catalyst; 6 mol % of olefins.
[c]*m*-Chloroperoxobenzoic acid (*m*-CPBA) were used as a terminal oxidant in the presence of *N*-methylmorpholine *N*-oxide additive.

al., 1997; Gravert and Griffin, 1993]. This result indicates that successful anchoring of chiral salen ligands onto the MCM-41 surfaces was achieved.

The three kinds of 3D structures of chiral salen ligands immobilized on MCM-41 are shown in Fig. 5. They reveal that the Mn center adopts a near planar geometry with phenyl groups in salicylaldehyde units. The presence of bulky groups in **Mn(III)-(A) and (B)/MCM-41** would prevent the substrate approach from the left and right sides of the complex. The substituents on the diimine bridge could lead to the more effective differentiation of substrate approaches. In the asymmetric epoxidation of olefins, the enantiofacial selection of corresponding (S)-epoxides to (S,S)-Mn(III) chiral salen complexes is observed and it can be explained by considering the favorable approaches of substrate through the open sites. The optimal design of salen structure is important to improve the enantioselectivity.

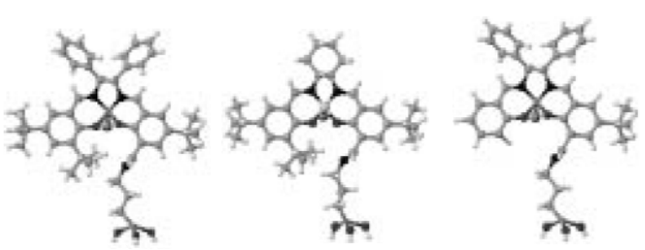


Fig. 5. The 3 dimensional structures of Mn(III)-(A)/MCM-41 (a), Mn(III)-(B)/MCM-41 (b) and Mn(III)-(A)/MCM-41 (c).

The enantioselective catalytic activities of the (salen)Mn(III) chloride complex immobilized on MCM-41 and the homogeneous complex of the same structure in solution were examined for the epoxidation of styrene, and the result is summarized in Table 1. Epoxidation reaction using a combined solution of *m*-CPBA/NMO was rapid even at −78 °C. The enantioselectivity was found to increase significantly at the low temperature. As shown in Table 1, a relatively high ee % value was obtained particularly over more hindered catalyst such as **Mn(III)-(A) and Mn(III)-(B)**. Especially, the reaction using heterogenized **Mn(III)-(A)/MCM-41** and **Mn(III)-(B)/MCM-41** gave a slightly improved selectivity as compared with homogeneous salen catalysts.

When the salen-immobilized MCM-41 was used as a catalyst, the pore size of mesoporous support had no effect on the catalytic activity for the asymmetric epoxidation. The conversion of styrene to epoxide was found to increase by using the MCM-41 which has a disordered pore system as compared with hydrothermally synthesized MCM-41. It is believed that the disordered pore system of MCM-41 synthesized by the solvent evaporation method has the advantage of three dimensional diffusion.

In the case of styrene epoxidation, the salen complexes synthesized from diphenylethylenediamine derivative such as **Mn(III)-**

Table 2. Asymmetric epoxidation of *trans*-β-methylstyrene on the heterogenized chiral Mn(III)-salen complexes

Entry	Catalyst	Reaction temp. (K)	Conversion (%)	ee (%)
1	Mn(III)-A	233	95	15
2	Mn(III)-A	290	98	10
3	Mn(III)-B	233	96	24
4	Mn(III)-A/MCM-41	233	83	13
5	Mn(III)-B/MCM-41	233	84	21

The same reaction conditions as shown in Table 1.

(A) and **-(C)** were more efficient catalysts than those obtained from cyclohexanediamine. Even though the catalyst of **Mn(III)-(C)** has a half-unit of simple salicylaldehyde, it gave a relatively high enantioselectivity in the asymmetric epoxidation. Furthermore, higher turnover number could be obtained over this unsymmetrical salen catalyst than over a symmetrical salen complex such as **Mn(III)-(A), Mn(II)-(B)**. The high asymmetry-inducing ability of unsymmetrical salen complex in this work is attributed to the intense interaction of the substituent of salen ligands near the metal center with incoming substrate.

The increase in the enantioselectivity over the homogeneous catalyst **Mn(III)-C** may be attributed to the presence of electro-donating methoxy groups. The immobilized chiral Mn salen/MCM-41 catalyst was also efficient in the epoxidation of *trans*-β-methylstyrene. The **Mn(III)-(A)** and **-(B)** catalyst exhibited a low enantioselectivity for the epoxidation of *trans*-β-methylstyrene. It has been known that the chiral salen Mn(III) complexes show low selectivity for the epoxidation of *trans*-olefins. Homogeneous chiral Mn(salen) complexes and heterogenized chiral salen Mn samples gave almost the same selectivity in this reaction. 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 exsist 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

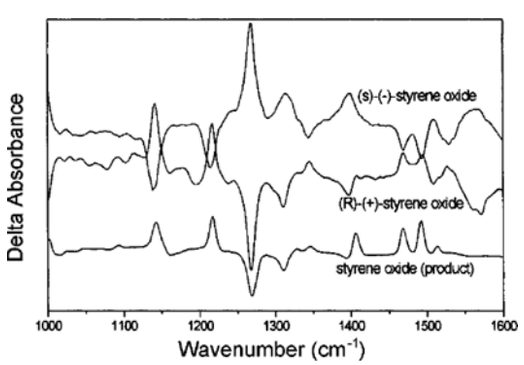


Fig. 6. VCD spectra of reference styrene oxides and a product.

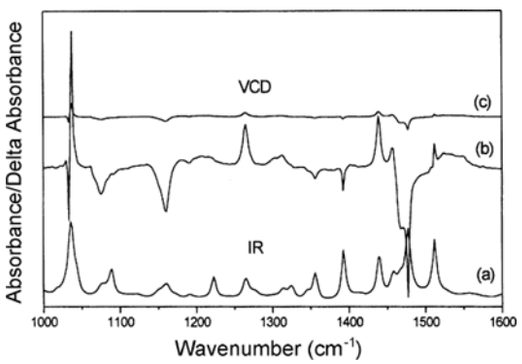


Fig. 7. IR and VCD spectrum of (1S, 2S)-(−)-1-phenylpropylene oxide (a, b) and VCD spectrum of the product oxide showing 10% ee (c).

the accurate estimation of enantiomeric excess and their absolute configurations [Spencer et al., 1990]. Optically pure samples were used as references to confirm the absolute configuration of the products. Three VCD spectra are shown in Fig. 6: one is a spectrum of 99% ee R(+)-styrene oxide obtained from Aldrich Co., another is that of 99% ee S(−)-styreneoxide and the other is that of the S(−)-styrene oxide obtained using the Mn(III) salen complex as a catalyst. The comparison between the values of % ee determined by VCD and those measured by GC are in very good agreement to within 2% ee. The VCD spectra of opposite configuration, such as R(+) and S(−), exhibited the reverse absorption peaks as shown in Fig. 6.

Fig. 7 shows the VCD spectra of the reference 99% (1S,2S)-(−)-1-phenylpropylene oxide and the product having 10% ee. The FT-IR spectrum is also shown in the same figure. These spectra have shown directly that the (S,S)-Mn(III) chiral salen complexes oxidized *trans*-β-methylstyrene to (S)-epoxides in the asymmetric epoxidation. It is very useful to determine the absolute configuration and % ee value by this VCD analysis for the asymmetric reactions.

CONCLUSION

Purely siliceous MCM-41 has been prepared by a solvent evaporation method and a hydrothermal synthesis using C_{16}TMABr and C_{22}TMACl surfactants as template, respectively. The mesoporous samples synthesized in ethanol solvent by using this evaporation method showed a fully disordered pore system, but those obtained by the hydrothermal synthesis had highly ordered pores. The mesoporous materials synthesized by the evaporation method exhibited a slightly broad pore size distribution. The new chiral salen complexes of different structures could be supported on the mesoporous MCM-41 through the condensation of 3-aminopropyltrimethoxysilane and 2,6-diformyl-4-*tert*-butylphenol. The asymmetric catalytic epoxidation using chiral (salen)complexes which are immobilized on MCM-41 could be applied with success, and high enantioselectivities were attainable in the epoxidation. 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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