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Catalysis Today 63 (2000) 537–547

CATALYSIS TODAY

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The catalytic activity of new chiral salen complexes immobilized on MCM-41 in the asymmetric hydrolysis of epoxides to diols

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Abstract

The synthesis of MCM-41 type mesoporous material has been performed by the solvent evaporation method. The chiral salen Co(III)(OAc) complexes are immobilized on a siliceous MCM-41 through the multi-step anchoring and applied as catalysts in the hydrolytic kinetic resolution of racemic epoxides to diols. The incorporation of salen complexes onto the mesoporous material is demonstrated by UV–Vis spectroscopy, and tested with the catalytic hydrolysis reaction. The chiral salen Co(III) complexes catalyze the hydrolysis of epichlorohydine, 1,2-epoxyhexane, epoxystyrene and epoxycyclohexane under very mild conditions. This reaction can proceed in acetonitrile and THF solvents.

Keywords: New chiral salen complexes; MCM-41; Asymmetric hydrolysis

1. Introduction

Recently, a family of mesoporous MCM-41s has received much attention and the synthesis and characterization of mesoporous silicas have been widely reported in the literature [1–4]. One of the MCM-41 members shows a uniform hexagonal array of mesopores, which is dependent on the template type and synthesis conditions. These MCM-41 can be prepared hydrothermally by addition of 1,3,5-trimethylbenzene (MS) as an auxiliary chemical. In this case, the pore size of MCM-41 increased upto 12 nm with increasing amount of MS. Namba et al. [5] have succeeded in the hydrothermal synthesis of highly ordered silica MCM-41 using *n*-cetyltrimethylammonium bromide (C_{16}TMABr) or *n*-docosyltrimethylammonium chloride (C_{22}TMACl) as templates by reducing the pH (pH = 9) at the beginning of reaction. Moreover, the pore size of MCM-41 has been finely controlled by using a mixture of C_{16}TMABr/C_{22}TMACl template. In this case, the pore size of obtained MCM-41 was from 1.8 to 4.2 nm. Recently, Roh et al. [6] have synthesized the mesoporous silica in acidic conditions by the 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 a mild reaction condition. As a result, hexagonal-arrayed powders could be successfully synthesized within 4 h.

To date, some kinds of approach have been adopted for the immobilization of chiral salens. The chiral Mn salen complexes have been supported on polymers in general. 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 [7,8]. The encapsulation of salen complex using ship-in-bottle

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0920-5861/00/$ – see front matter
PII: S0920-5861(00)00501-0

method was also applied [9,10]. In addition, Mn salen ligands were immobilized by ion exchange reactions [11–13]. Frunza et al. [13] have investigated the embedding of enantioselective homogeneous chiral Mn(III) cationic salen complexes into the pore of mesoporous MCM-41 materials. Very few asymmetric catalytic reactions have been examined using chiral salen complexes immobilized on MCM-41. We have recently reported the new approach of sequent anchoring method, reacting a functionalized ligand with reactive groups of inorganic compounds, such as MCM-41, step-by-step [14].

In this work, we have synthesized the siliceous and Al-containing MCM-41s by a fast solvent evaporation method using C_{22}TMACl surfactant as a template and used this mesoporous material to immobilize the new chiral salen complexes on it by a new grafting method using 3-aminopropyltrimethoxysilane and 2,6-diformyl-4-*tert*-butylphenol. By applying this new grafting method using a diformylphenol as a building block of salen structure, it is possible to synthesize various unsymmetrical chiral salens of different structure. In addition, we report herein that the enantioselective diols have been synthesized from racemic epoxides on the heterogenized chiral salen Co(III)(OAc) complexes, and these new catalysts afford high level of enantioselectivity in the asymmetric hydrolytic resolution reaction. Tokunaga et al. [15] have described a practical route to enantiomerically enriched terminal epoxides by way of a hydrolytic kinetic resolution using chiral Co(III)(OAc) salen catalysts. It is an attractive method to synthesize the 1,2-diols in high enantiomeric excess (ee) from the cheap racemic epoxides. 1,2-diols generated by epoxide hydrolysis are known as valuable chiral building blocks for organic synthesis.

2. Experimental

2.1. Preparation of MCM-41

A purely siliceous MCM-41 was synthesized according to the solvent evaporation method as reported by Roh et al. [6]. The Si-MCM-41 of very high crystallinity could be synthesized within 4 h by this modified method. The synthesis procedure of mesoporous Si-MCM-41 is depicted in Fig. 1. Ethanol and methanol were used as solvents, respectively. The calculated amount of tetraethylorthosilicate (TEOS; Aldrich) was put into the ethanol solution and stirred vigorously for 15 min. A pure water was added to this mixture and it was heated to reflux (60°C). HCl was added dropwise and the mixture was vigorously stirred for 90 min. The typical mole ratio of TEOS:EtOH (or MeOH):H_2O:HCl was 1×10^{-2}:3×10^{-2}:8×10^{-2}:5×10^{-2}. The reactant mixture was cooled to 25°C and then stirred again for 30 min. The sample was aged at 50°C for 15 min without agitation. The mixture was diluted with a dehydrated ethanol and C_{22}TMACl (Arquad 22–80, Lion) or C_{16}TMABr (Aldrich) was dissolved in the resulting solution. 1,3,5-trimethylbenzene (TMB) was added as an auxiliary chemical in this step (TMB/TEOS, mole ratio = 3). After stirring for 30 min, the solvent was evaporated at 60°C. The resultant dried solid was heated to 540°C at the heating rate of 1°C/min and then calcined at 540°C in air for 6 h. In addition, Al-containing MCM-41 was synthesized and used as a support for loading the salen complexes on it. Aluminum isopropoxide was used as an Al source and it was added to TEOS solution at the first step of hydrolysis. The next procedure was same as the method mentioned in Fig. 1.

The synthesized MCM-41 samples were characterized by X-ray diffraction (XRD) analysis (Phillips PW 3123) and N_2 adsorption for the determination of pore size distribution (BJH method) using a Micrometrics ASAP 2000 automatic analyzer. UV–Vis spectroscopic measurements were carried out using Varian CARY 3E double beam spectrometer in the range 190–820 nm.

2.2. Immobilization of chiral salen ligands on MCM-41

First, the chiral salen complexes were immobilized onto the MCM-41 by the new multi-grafting method reported in the previous paper [14]. A suspension of 6 g of 3-aminopropyltrimethoxysilane and 20 g of MCM-41 in 100 ml of toluene was heated to reflux with stirring. After heating for 6 h, the powder sample was filtered and washed with diethylether. The 2,6-diformylphenol was synthesized by three-step procedure from 2,6-dimethylphenol with high yield and good reproducibility as reported by Zondervan et al.

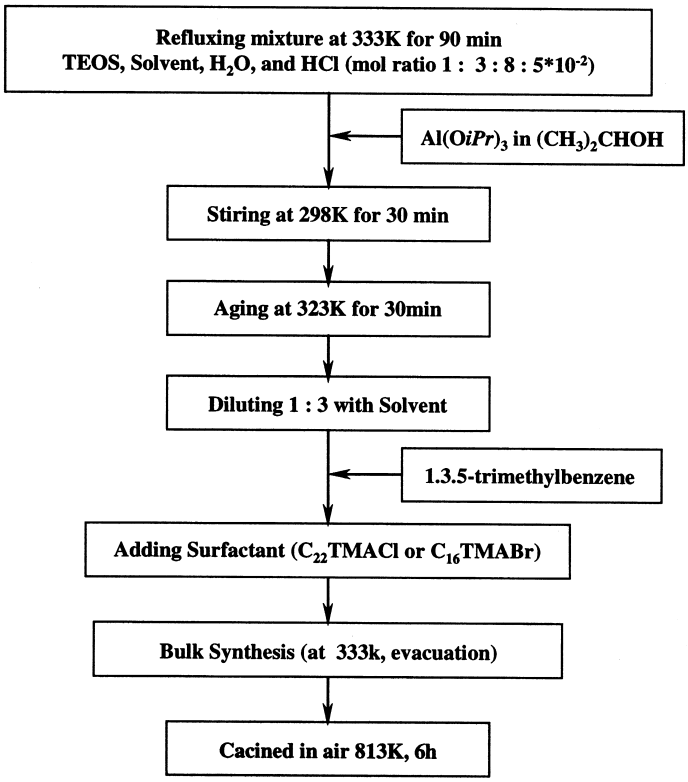
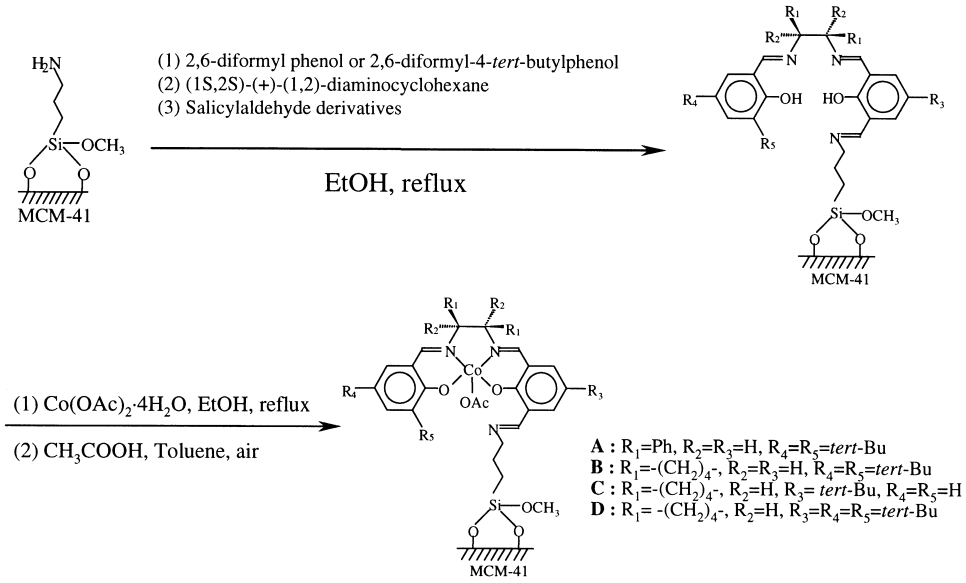


Fig. 1. Schematic diagram for the synthesis of MCM-41 by a solvent evaporation method.

[16]. The compound of 4-*tert*-butyl-2,6-diformylphenol was synthesized according to the procedure described by Chang et al. [17]. These diformylphenols were reacted with the previously obtained 3-aminopropyl silylfunctionalised MCM-41 in a refluxing ethanol solution for 10 h, respectively. One aldehyde group in the diformylphenol derivative reacts with the amino group of 3-aminopropylsilane immobilized on MCM-41. After cooling, the powder was collected by filtration, washed with diethylether and methanol. The condensation of remaining aldehyde with one amino group in the available chiral auxiliary (1*S*,2*S*)-(+)-1,2-diaminocyclohexane has occurred and the sequent condensation of the other amino group in diaminocyclohexane with the corresponding excess salicylaldehyde derivatives (salicylaldehyde or 2,4-di-*tert*-butyl salicylaldehyde) in a refluxing ethanol has resulted in the formation of chiral salen ligands (3.6 wt.% loading) on MCM-41 as shown in Scheme 1. The chiral salen Co(II) complexes immobilized MCM-41 was readily accomplished by refluxing an ethanolic solution of a salen ligand with excess Co(II) acetate tetrahydrate in air for 2 h. Then, after washing, the dried powder was treated with a dehydrated acetic acid in toluene at room temperature for 2 h. The resulting dark brown powder was filtered and washed several times with dichloromethane and methanol.

In the second process, Al-containing MCM-41 was used to immobilize the chiral salens on it. Al-MCM-41 was ion exchanged with $Co(OAc)_2$ at 80°C for 24 h, before being filtered, washed with distilled water, and then vacuum dried. The Si/Al ratio of the obtained sample was 46. The calcined Co(II)-ion exchanged Al-MCM-41 was then refluxed with the chiral salen ligand having the same structure of catalyst E (see



Scheme 1.

Scheme 2) in toluene for 24 h, cooled and washed with ethanol. This sample was later dried at 130°C for 6 h, resulting in the immobilization of 1.4 wt.% chiral salen complexes. The catalyst obtained by this ion exchange method would be denoted as *(E)-ion ex*.

In the third process, the chiral salen ligand E was supported on H type Al-MCM-41 by impregnation. The desired amount of chiral salen complex was dissolved in dichloromethane and then the dried Al-MCM-41 (500 mg) was added to the solution. The mixture was heated to reflux for 24 h in ethanol solvent. The powder sample was then filtered and washed with dichloromethane. The resulting maximum amount of salen complex loaded on MCM-41 was 5.7 wt.%. The catalyst obtained by the impregnation method is denoted as *(E)-imp*.

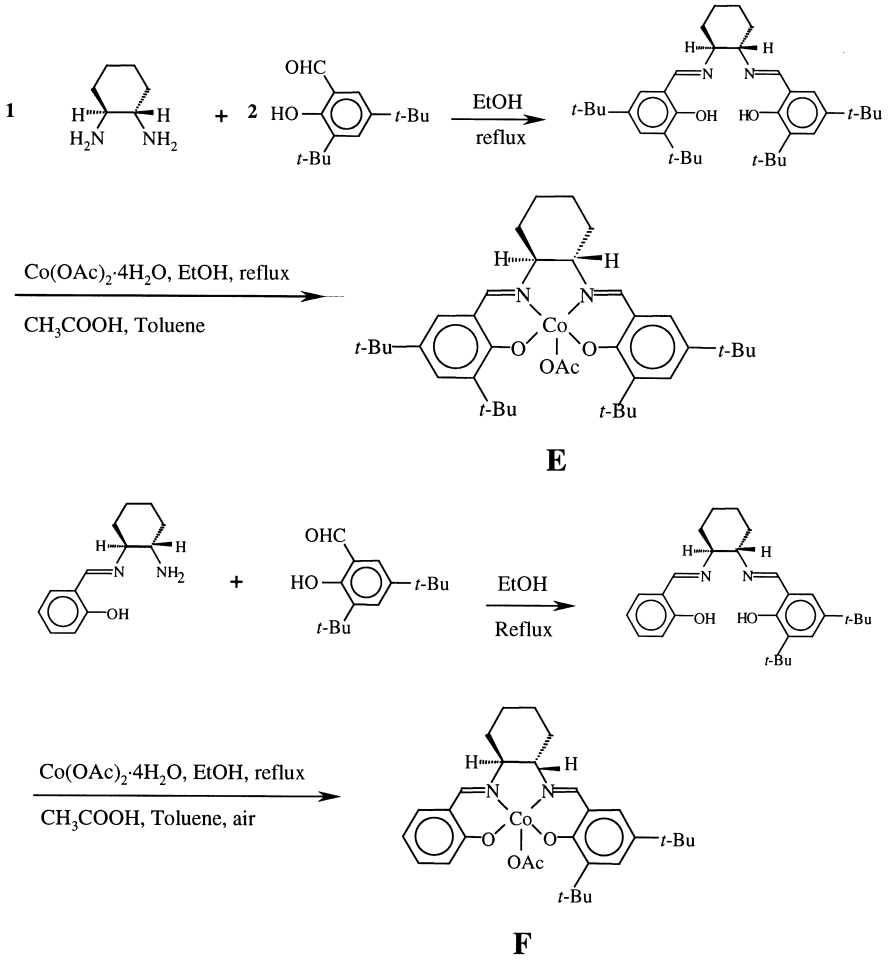
In addition, the conventional homogeneous chiral salen ligands [18] were also synthesized and used as catalysts to compare the catalytic activities and to evaluate the relations between the structural features of salen ligands and enantioselectivity. The molecular structures of these homogeneous complexes, used in the catalytic reaction, are shown in Scheme 2.

2.3. The hydrolytic kinetic resolution of racemic epoxides to diols

The general procedure of asymmetric hydrolysis is as follows. A mixture of chiral salen Co(III)(OAc) complex (0.05 mmol) and a racemic epoxide (10 mmol) was stirred for 10 min. 5.5 mmol H_2O was added in one portion and the reaction was performed at room temperature for 12–48 h. The reaction vessel was cooled in an ice bath during the water addition to limit the loss of substrate as a result of evaporation. After filtration to remove the solid catalysts, the diol was then distilled under vacuum and isolated as a viscous liquid or a crystal powder. 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).

3. Results and discussion

The MCM-41 type mesoporous materials were characterized by XRD analysis and the results of XRD patterns are given in Fig. 2. C_{16}TMABr and



Scheme 2.

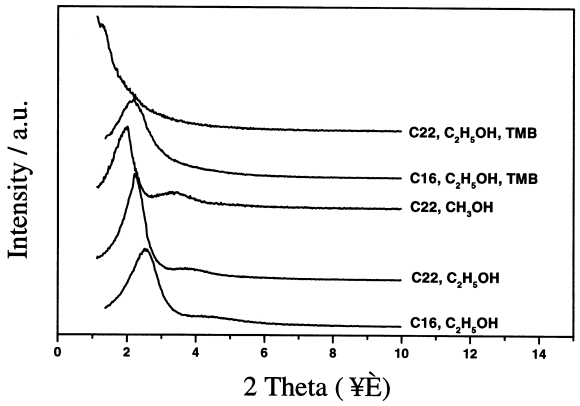


Fig. 2. XRD patterns of MCM-41 obtained under the various synthesis conditions.

C_{22}TMACl were used as the templates. The (1 0 0) diffraction peak of Si-MCM-41 shifted to the low 2θ value when the sample was synthesized by using C_{22}TMACl surfactant, indicating a significant lattice expansion. The (1 1 0) and (2 0 0) reflections of MCM-41, obtained by the solvent evaporation method, were very weak and broad as compared to that synthesized hydrothermally. The calculated d_{100}-spacings of calcined MCM-41 were 4.7 and 3.7 nm. The 2θ values decreased by the addition of TMB, showing the pore enlargement also.

The pore size distributions of Si-MCM-41 synthesized in this work are shown in Fig. 3. All mesoporous samples showed a sharp distribution in the pore size without addition of TMB and the use of methanol sol-

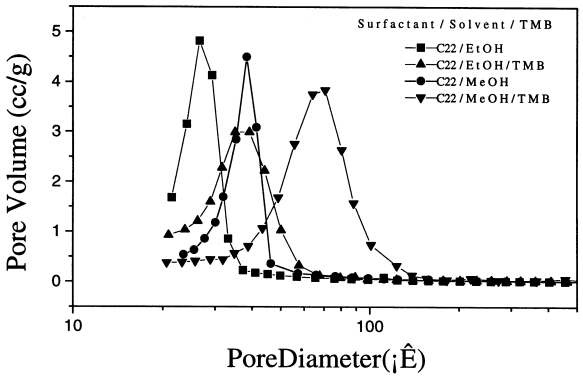


Fig. 3. BJH pore size distributions of MCM-41 obtained by using C_{16}TMABr and C_{22}TMACl templates, and TMB.

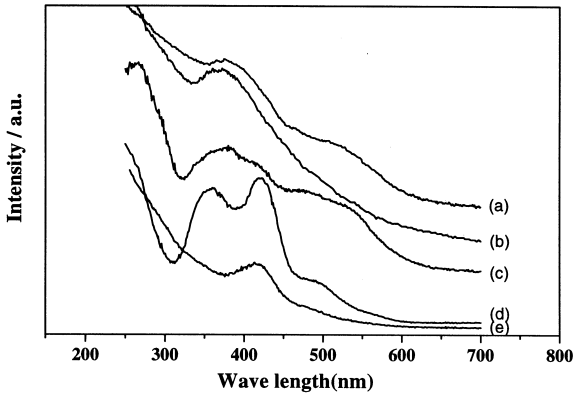


Fig. 5. Diffuse reflectance UV–Vis spectra of various chiral salen catalysts: (a) Co(II) salen on MCM-41; (b) Co(III) salen on MCM-41; (c) after reaction; (d) homogeneous Co(II) salen; (e) homogeneous Co(III) salen.

vent resulted in the expansion of pore channel size. The average pore sizes determined by N_2 adsorption were 4.0 and 2.8 nm when the added solvents were methanol and ethanol, respectively. In this case, the surfactant was C_{22}TMACl. In addition, the BJH pore size of MCM-41 increased with addition of TMB. The regular pore size was 7.5 nm by using TMB as an auxiliary chemical in methanol solvent. By addition of TMB in the solvent evaporation synthesis of MCM-41, the pore size distribution of calcined samples became broad. Si-MCM-41 could be synthesized with a high crystallinity within 4 h by the evaporation method and the pore size could be controlled by the addition of TMB in this work.

Fig. 4 shows the TEM images of purely siliceous MCM-41. These samples were obtained using C_{22}TMACl surfactant. The MCM-41 prepared in the ethanol solvent exhibited a fully disordered channel structure. But the regular pore structure was obtained when the ethanol solution was used as a solvent. The MCM-41 samples having an disordered pore system (mean pore size 38 Å) were used to immobilize the chiral salen complexes onto it by the procedure as shown in Scheme 1.

UV spectroscopy can be used as a sensitive probe to detect the presence of cobalt salen complexes. The

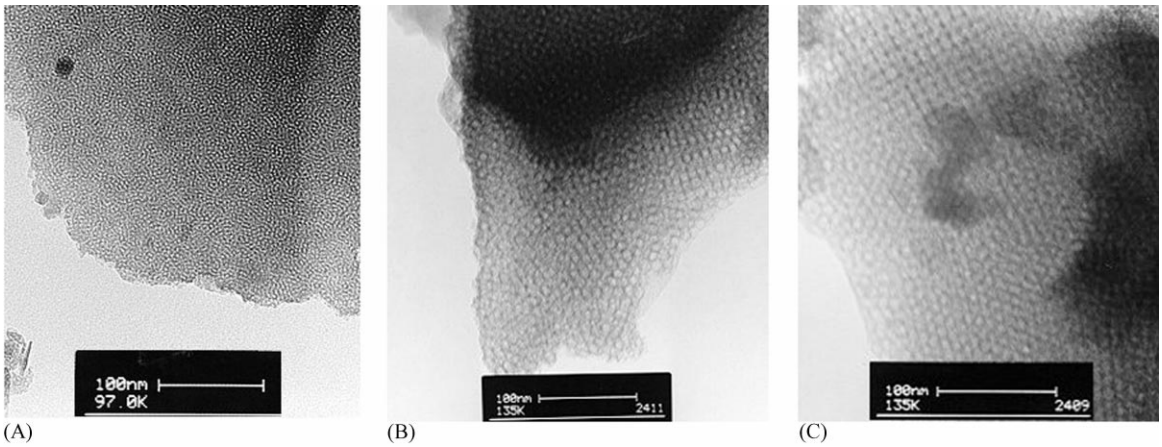
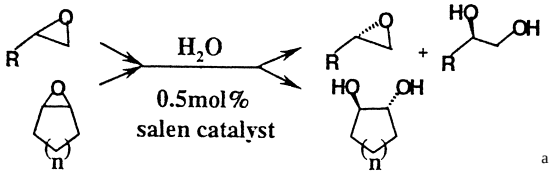


Fig. 4. TEM images of Si-MCM-41 and Al-MCM-41 obtained by the solvent evaporation method: (A) C_{22}TMACl/ethanol solvent (Al-MCM-41); (B) C_{22}TMACl/methanol solvent (Si-MCM-41); (C) C_{22}TMACl/methanol solvent/TMB addition (Si-MCM-41).

chiral salen Co(III)(OAc) complexes immobilized on MCM-41 have been characterized by diffuse reflectance UV spectroscopy and the typical UV–Vis spectra are given in Fig. 5. The homogeneous chiral salen ligands of Co(II) form showed the broad bands at near both 400 and 500 nm. After oxidizing the Co(II) salens by air in the presence of acetic acid, generating the corresponding Co(III)(OAc) complexes, 500 nm peak on the UV spectra has disappeared. The salen complexes immobilized on MCM-41 showed the same phenomena on the UV spectra. The broad band at 400 nm is probably due to charge-transfer transition between the metal and ligand. This result indicates that the successful anchoring of chiral salen ligands onto the MCM-41 surfaces achieved. It is found that the homogeneous chiral Co(III)(OAc) salen complexes as well as the immobilized ones have reduced to Co(II) form during the hydrolysis reaction, showing the UV absorption band at 500 nm after reaction. These reduced complexes were regenerated by treatment with acetic acid in air.

The catalytic activity and enantioselectivity of the Co(III)(OAc) salen complexes immobilized on MCM-41 and the homogeneous complexes were examined for the hydrolysis of epoxides. Epichlorohydrine, 1,2-epoxyhexane and epoxystyrene of racemic form were hydrolyzed over various homogeneous and heterogenized chiral salen catalysts at 20°C with

Table 1
Hydrolytic ring-opening of terminal- and meso-epoxide with water catalyzed by the immobilized chiral Co(III) salens



[a]

Entry	Catalyst	Substrate	Time (h)	Solvent	Diol yield (%)	ee(%) of diol
1	A	Epichlorohydrine	24	None	Trace	–
2	B	Epichlorohydrine	24	None	34	86
3	C	Epichlorohydrine	24	None	35	92
4	D	Epichlorohydrine	24	None	31	87
5	E	Epichlorohydrine	12	None	36	86
6	E	Epichlorohydrine	12	THF	34	86
7	E	Epichlorohydrine	12	Acetonitrile	18	85
8	F	Epichlorohydrine	12	None	34	90
9	A	Styrene oxide	48	None	Trace	–
10	B	Styrene oxide	48	None	33	98
11	C	Styrene oxide	48	None	35	97
12	E	Styrene oxide	24	None	38	98
13	F	Styrene oxide	24	None	35	97
14	B	1,2-Epoxyhexane	24	None	42	97
15	D	1,2-Epoxyhexane	24	None	38	96
16	E	1,2-Epoxyhexane	12	None	46	98
17	B	Epoxycyclohexane	24	None	34	83
18	D	Epoxycyclohexane	24	None	29	83
19	D	Epoxycyclohexane	24	MeOH	11	82
20	D	Epoxycyclohexane	24	THF	37	83
21	F	Epoxycyclohexane	24	None	39	84
22	B	Epoxycyclopentane	48	None	20	62
23	D	Epoxycyclopentane	48	None	18	61
24	D	Epoxycyclopentane	48	MeOH	7	60
25	D	Epoxycyclopentane	48	THF	29	62
26	F	Epoxycyclopentane	48	None	39	64

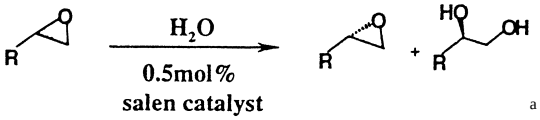
[a] Olefin,10 mmol; water, 5.5 mmol; chiral salen catalyst, 0.5 mol%; reaction temperature, 20°C.

or without addition of solvents. By using (*S*,*S*)-form salen catalysts, *R*-epoxide in racemates was selectively catalyzed to *R*-diol and as a result, *S*-epoxide remained in the final product mixture. Epichlorohydrine, 1,2-epoxyhexane and epoxystyrene gave a very high diol yield and ee% over the chiral Co(III)(OAc) salen complex, respectively.

The effects of salen structure and solvent added on the catalytic activity and enantioselectivity have been investigated and the results are summarized in Table 1. The catalysts of unsymmetrical-type salens (B, C and F) which have less steric hindrance, showed unexpectedly higher ee% value of diols than the conventional symmetrical salens having two *tert*-butyl groups at the para and ortho-position to the salen oxygens. The unsymmetrical Co(III)(OAc) salen catalyst exhibited the enantioselectivity of 92 and 98 ee% in the hydrolysis of epichlorohydrine and epoxystyrene, respectively. The reaction using the immobilized Co(III)(OAc) salen/ MCM-41 gave the almost same enantioselectivity as compared to that of homogeneous salen catalysts. But the reaction rate was low, so that the prolonged reaction time was required, when the chiral salen complexes immobilized on MCM-41 was used as a hydrolysis catalyst. The Co(III)(OAc) salen complexes synthesized from (-)-1,2-diphenylethylenediamine derivatives exhibited no catalytic activity for this reaction. In efforts to extend this reaction to the hydrolysis of meso epoxides, the synthesis of cyclohexanediol and cyclopentanediol from the corresponding cyclo-epoxide was carried out. The reaction was found to be applicable to a series of other meso epoxides. This diol synthesis reaction was performed using a homogeneous salen Co(III)(OAc) catalyst system and the chiral salens immobilized on Si-MCM-41, respectively. The enantioselectivities of several Co(III)(OAc) salen complexes immobilized on MCM-41 were compared and found to be similar in the hydrolytic resolution of terminal and meso epoxides. By applying the immobilized salen catalysts, the product separation became easier and the catalyst could be recycled without observable loss in activity.

The results obtained in the hydrolysis of meso epoxides are also listed in Table 1. The ring opening reaction with water was effected by the kind of solvents. Although reactant epoxides are immisible with water, the terminal- and meso epoxides were also readily catalyzed by the Co(III)(OAc) salen complexes at room temperature in the solvent-free system. By addition of solvents, the reaction mixture became homogeneous. THF was found as the most effective solvent in the hydrolytic ring opening of epoxides by means of catalytic hydrolysis. No measurable changes in the enantioselectivity and the reaction rate were found by using THF as a solvent in the hydrolysis of meso epoxides. The use of methanol and acetonitrile solvents displayed a low level of reactivity, leading to the low diol yield. But the enantioselectivity was not

Table 2
The effect of catalyst preparation method on the catalytic activity in the hydrolytic ring-opening of terminal epoxides with water



[a]

Entry	Catalyst	Substrate	Time (h)	Diol yield (%)	ee(%) of diol
1	D	Epichlorohydrine	24	31	87
2	E	Epichlorohydrine	12	36	86
3	(E)-ion ex	Epichlorohydrine	24	28	80
4	(E)-imp (1.5)	Epichlorohydrine	24	34	41
5	(E)-imp (3.5)	Epichlorohydrine	24	35	62
6	(E)-imp (5.7)	Epichlorohydrine	24	32	78
7	E	Styrene oxide	24	38	98
8	(E)-ion ex	Styrene oxide	48	27	91
9	(E)-imp (1.5)	Styrene oxide	48	30	49
10	(E)-imp (5.7)	Styrene oxide	48	28	88

[a] Olefin,10 mmol; water, 5.5 mmol; chiral salen catalyst, 0.5 mol%; reaction temperature, 20°C.

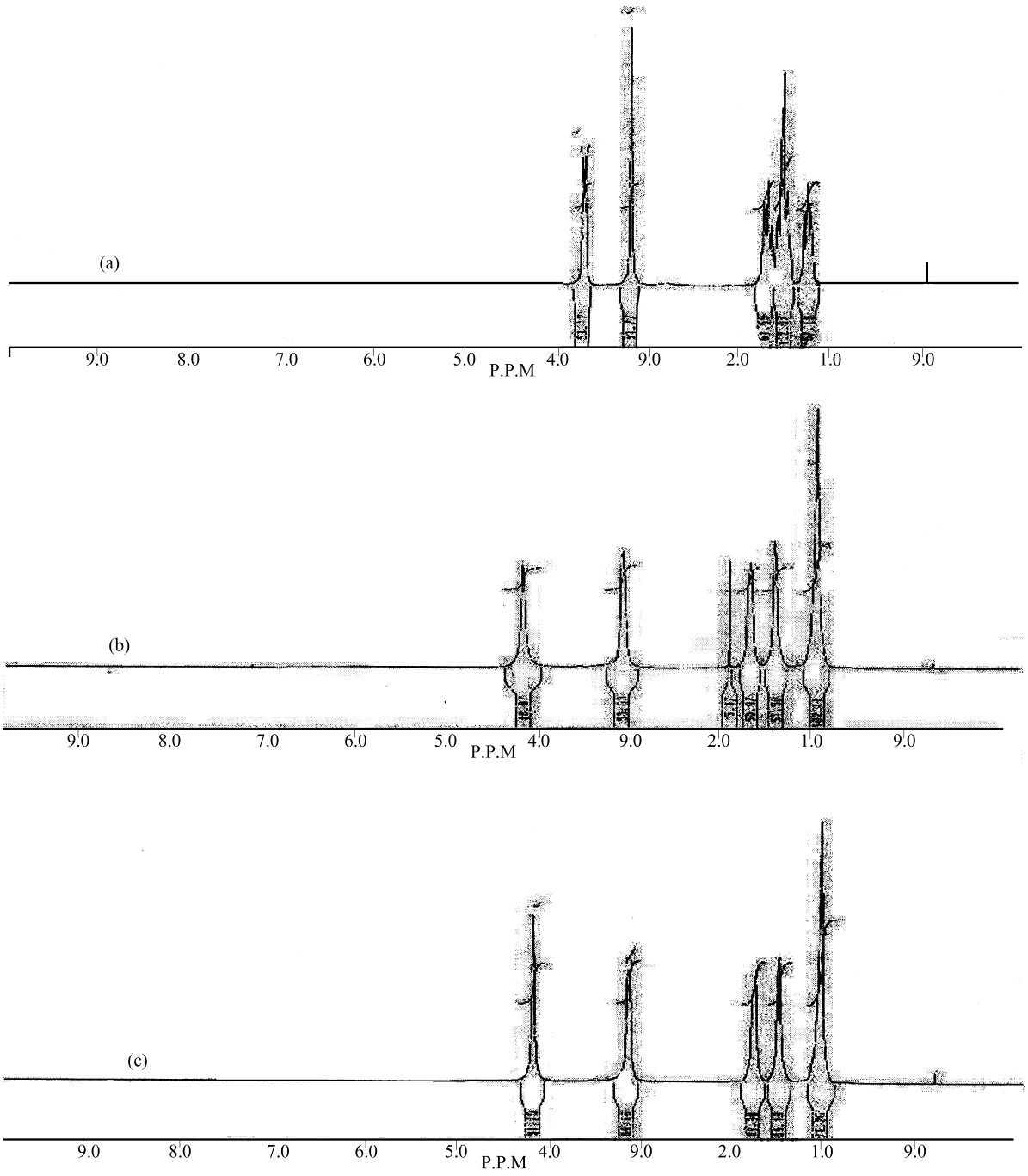


Fig. 6. H-NMR spectra of pure (a) *cis*-1,2-cyclohexanediol product (b) 1,2-cyclohexanediol and (c) *trans*-1,2-cyclohexanediol.

dependent on the presence of solvents. For example, as shown in Table 1, (1*R*,2*R*)-*trans*-1,2-cyclohexanediol was obtained in 80 and 29% yield over the catalyst without any solvents addition. The reaction in a methanol solvent took place with a lower cyclohexanediol yield of 11%, but with the same enantioselectivity. The chiral salen Co(III)(OAc) complexes were readily reduced to a Co(II) form during the hydrolysis reaction in the methanol and acetonitrile solvents, except THF. These phenomena were confirmed by UV–Vis analysis.

It was convenient to carry out the hydrolysis reaction in the absence of a solvent using the heterogenized salen complexes. Because the powder catalysts could be recycled by washing it with a CH_2Cl_2 solvent and treating with acetic acid in air at room temperature. After using Co(salen) complexes immobilized on MCM-41 as catalysts, the resultant solution exhibited no color and no Co metal ion was detected in the solution. This means that Co(salen) complexes immobilized on mesoporous materials are stable during the reaction and exist in the pore system without any extraction.

As can be seen in Table 2, Co(III)-(*E*)-imp type salen catalysts have exhibited lower enantioselectivity to diol than the other chiral salen complexes immobilized by the multi-step anchoring or by the ion-exchange method. Over this impregnation type catalyst, the enantioselectivity to diol were increased as the increasing the amount of Co(III)(OAc) salen complexes, as expected. This result suggests that the Co(III)(OAc) complexes may be bound to the proton of Al-MCM-41 via imine groups of salen. It is known that imine groups can be protonated and immobilized on Al-MCM-41 [13]. When the loading amount of salen complexes is low, the free protons on MCM-41 can lead to the hydrolytic ring opening of epoxide and the formation of racemic diols, resulting in the decrease of enantioselectivity. In addition, small amounts of salen complexes, which were impregnated on a proton type Al-MCM-41, were leached out during the catalytic reaction. As reported by Herron [19], the salen ligand possesses two ionizable protons that are lost during complexation to a cobalt ion; thus, coordination to a divalent cation will result in the production of an electrically neutral complex and the liberation of two protons. Therefore, the released protons would become the charge compensators of the anionic zeolite framework, replacing the divalent Co ion in this capacity. As a result, Co(III)(OAc) salen complexes obtained by the complexation of salen ligand after Co ion-exchange may be placed in the same conditions as impregnated Co(III) salen complexes on the proton type Al-MCM-41. The Co(III)(OAc) salen complex prepared by the ion-exchange method showed almost the same catalytic properties as compared with that obtained by the impregnation method. Some salen complexes were dissolved into the reaction solvent from the MCM-41 support when the Co(III)(OAc) salen complex prepared by the ion-exchange method was used as a catalysts in the hydrolysis of epoxides.

The diol product obtained in this reaction was only the *trans*-1,2-cyclohexanediol. The peaks for *cis*-cyclohexanediol were not detected on the H-NMR spectra of obtained cyclohexanediol crystal products. The H-NMR spectrum of product 1,2-cyclohexanediol is compared with the pure reference *cis*- and *trans*-1,2-cyclohexanediol and these spectra are shown in Fig. 6.

The vibrational circular dichroism (VCD) spectroscopy was used to elucidate the stereochemistries of chiral molecules, including the accurate estimation of enantiomeric excess and their absolute configurations. Optically pure samples as well as a racemic sample were used as a reference to compare the VCD spectra. This VCD analysis is found to be very convenient to determine the absolute configuration and ee% value directly for the crystal powder samples obtained in the hydrolysis of epoxystyrene and epoxycyclohexane. The VCD spectra of opposite configuration, such as (1*R*,2*R*) and (1*S*,2*S*) exhibited the reverse absorbtion peaks.

4. Conclusions

In conclusion, the new chiral (salen) Co(III) complexes immobilized on MCM-41 could be synthesized by the multi-grafting method. The asymmetric hydrolysis of the terminal and meso epoxides to diols using the heterogenized catalysts can be applied with success. An unexpectedly high enantioselectivity was attainable on the Co(III) salen catalysts of unsymmetrical structures. On the basis of asymmetric hydrolytic resolution of various epoxides, the chiral

(salen) complexes immobilized on mesoporous material by the present procedure can be applied as an effective heterogenized homogeneous catalyst for the asymmetric reactions.

Acknowledgements

The authors gratefully acknowledge the financial support (1998) from Inha University.

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