The synthesis of new chiral salen complexes immobilized on MCM-41 by grafting and their catalytic activity in the asymmetric borohydride reduction of ketones

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The new chiral salen complexes were synthesized and supported on mesoporous MCM-41 through the condensation of 3-aminopropyltrimethoxysilane and 2,6-diformyl-4-*tert*-butylphenol by the multi-grafting method. The immobilized optically active Co(II) salen complexes showed a very high enantioselectivity in the asymmetric borohydride reduction of aromatic ketones. The chiral salen Co(II) complexes immobilized over MCM-41 were stable during the reaction and exhibited a relatively high enantioselectivity for the reduction of ketones as compared with the homogeneous salen catalysts.

Keywords: MCM-41, immobilization, grafting, chiral salen, reduction, 2,6-diformyl-4-*tert*-butylphenol

1. Introduction

Chiral (salen) Mn(III) complexes have been found to be highly enantioselective for the asymmetric epoxidation of conjugated *cis*-disubstituted and trisubstituted olefins [1–3]. The increasing interest towards this reaction brought some authors to develop the heterogeneous chiral Mn(III) salen catalysts. However, to date three kinds of approach have been adopted:

First, chiral Mn salen complexes were supported on polymers. As an application, Janssen et al. [4] have synthesized a dimeric form of (salen) Mn(III) ligand and retained this complex in the cross-linked polymer membrane to use as a catalyst for epoxidation. Minutolo et al. [5] have synthesized the polymer-bound chiral salen Mn(III) complex by copolymerization of salen complex with styrene and divinylbenzene. They showed the catalyst could effectively be recovered and reused several times without loss of activity and stereoselectivity. Breysse et al. [6] also heterogenized the chiral salen complex by a similar copolymerization reaction. Second, the encapsulation of salen complex using the ship-in-bottle method was applied. Sabater et al. [7] 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 the chloride complex in the homogeneous phase. Ogunwumi and Bein [8] 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 catalysts produced a high enantiomeric excess in the epoxidation of aromatic alkenes with NaOCl. Third, Mn salen ligands were immobilized by ion-exchange reaction. Piaggio et al. [9] reported that the Mn-exchanged MCM-41 modified with a chiral salen was an effective catalyst for the epoxidation of *cis*-stilbene. We also have immobilized the cationic type chiral Mn(III) salen complexes into the Al-MCM-41 by ion exchange [10]. Recently, Frunza et al. [11] 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 a chiral salen complex immobilized on MCM-41. As introduced by some authors, the immobilized chiral salen has been obtained only by the condensation of unsaturated olefin groups in salen structure with styrene and divinylbenzene. But the sequent anchoring method of reacting a functionalized ligand with reactive groups of organic and inorganic compounds (MCM-41), step by step, has not been reported yet. Here, we demonstrate the synthesis of the heterogenized chiral salen catalyst on the siliceous MCM-41 by a new grafting method using 3-aminopropyltrimethoxysilane and 2,6-diformyl-4-*tert*-butylphenol. This grafting method gives the advantage that the ligand preferentially binds at locations on the MCM-41 surface accessible for the substrate during a catalytic reaction. In addition, by this new grafting method using diformylphenol as a building block of the salen structure, it is possible to synthesize the various unsymmetrical chiral salens of different structure and to immobilize them over inorganic supports such as MCM-41 and silica. No attempt has been made to synthesize the grafted unsymmetrical salen complexes. We also report herein that these new catalysts afford a high level of enantioselectivity in the asymmetric reduction of α-tetralone and acetophenone with sodium borohydride.

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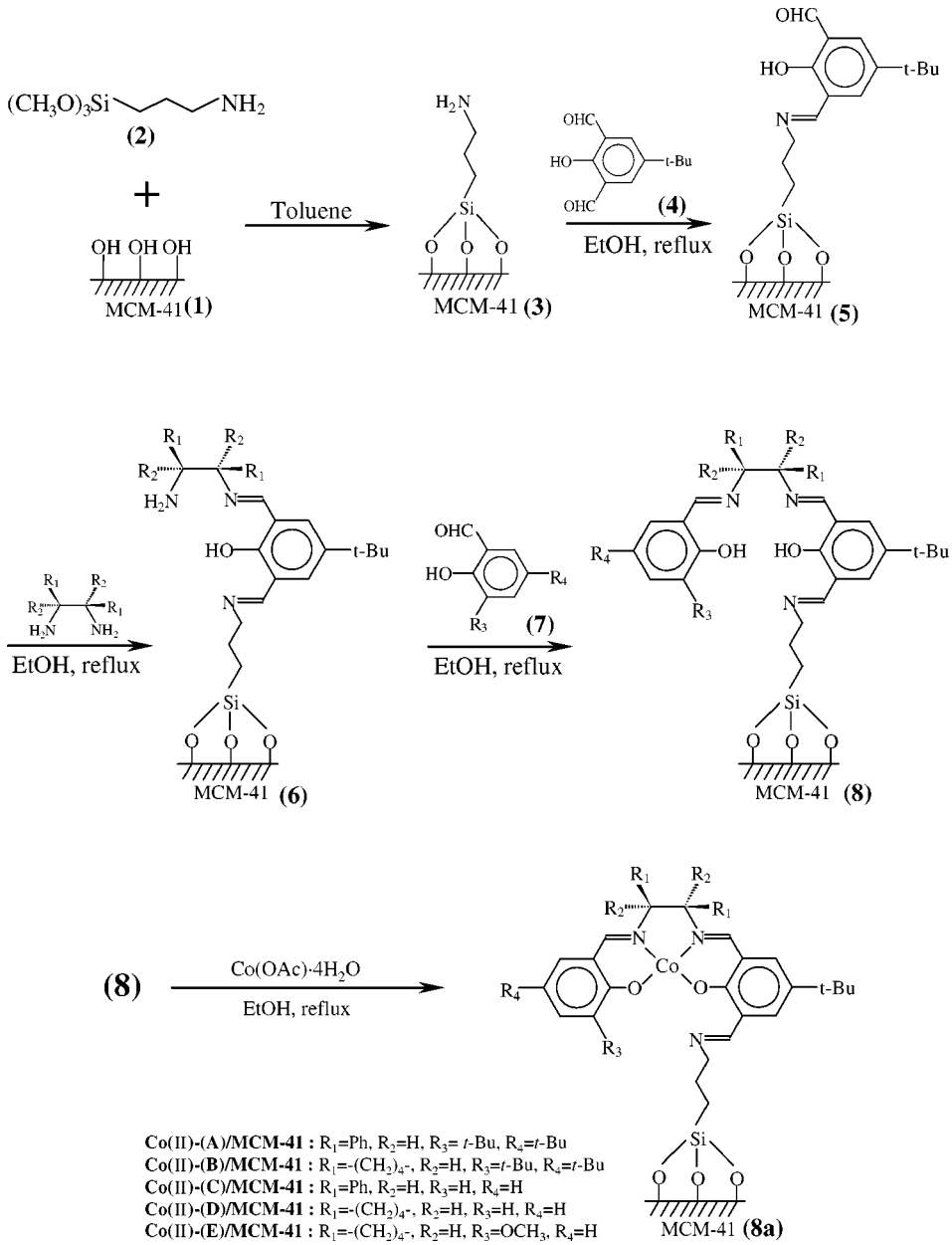


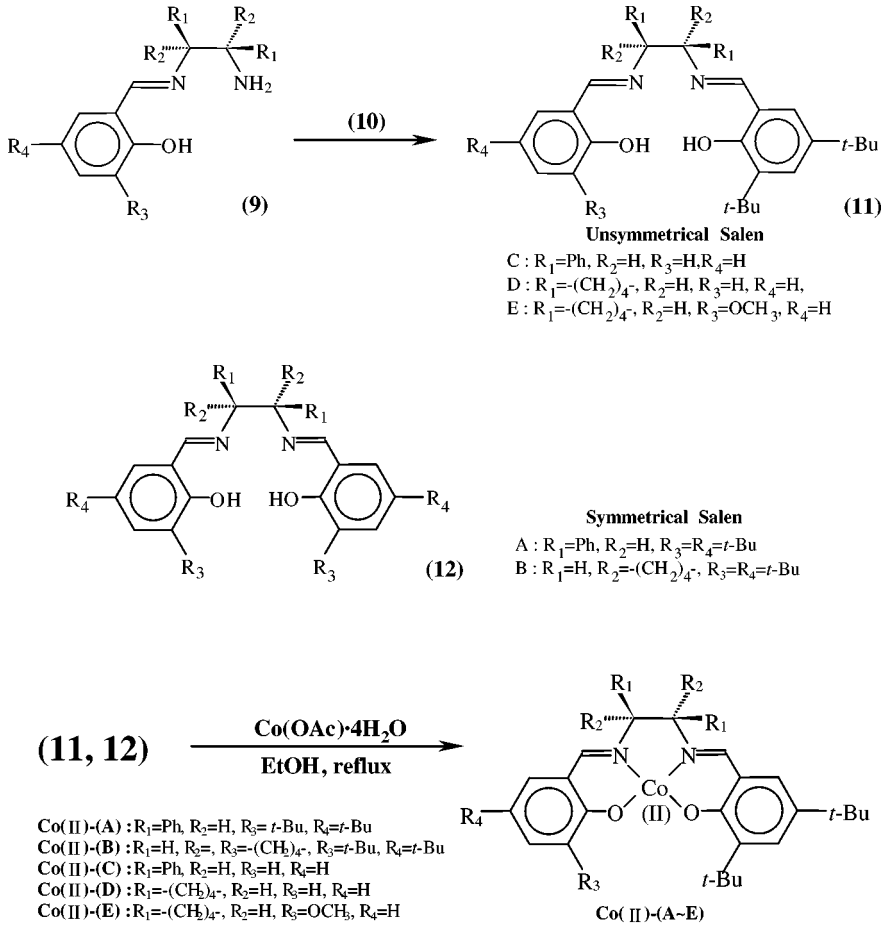
Scheme 1. The procedure for the synthesis of chiral salen complexes immobilized on MCM-41.

2. Experimental

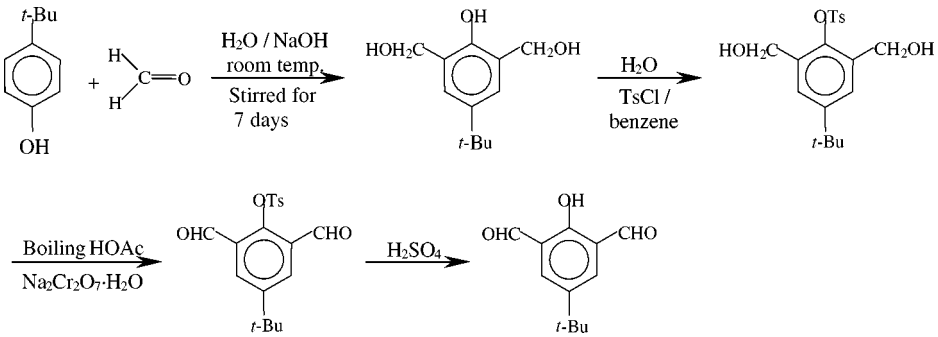
For this study, the chiral salen complexes were synthesized and immobilized on MCM-41 by the grafting method according to the procedure as shown in scheme 1. In addition, homogeneous symmetrical and unsymmetrical chiral salen complexes of the similar structure to the immobilized ones were synthesized to compare the enantioselectivity in the reactions. The synthesis procedure for homogeneous complexes is also shown in scheme 2.

2.1. Preparation of MCM-41 (1)

A purely silicious MCM-41 was synthesized according to the following procedure. The MCM-41 of very high crystallinity could be synthesized within 12 h by this modified method. Tetraethylorthosilicate (TEOS, 50 g) and ethanol (33 g) were added to pure water (35 g) and this mixture was heated to reflux (60 °C) for 10 min. 1.25 g HCl was added dropwise and the mixture was vigorously stirred for 90 min. The mole ratio of TEOS: $EtOH : H_2O : HCl$ was $1 : 3 : 8 : 5 \times 10^{-2}$. The reactant mixture was cooled to 25 °C and then stirred again for 30 min. The sample was aged at 50 °C for 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) was dissolved in the resulting solution. C_{22}TMACl was used as a template. After stirring 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.



Scheme 2. The procedure for the synthesis of homogeneous chiral salen complexes.



Scheme 3.

*2.2. Preparation of 3-aminopropylsilyl-functionalised MCM-41 (**3**)*

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

*2.3. Preparation of 2,6-diformyl-4-tert-butylphenol (**4**)*

4 was synthesized according to the procedure described by Chang et al. [12] (scheme 3).

*2.4. Reaction of 2,6-diformyl-4-tert-butylphenol with 3-aminopropylsilyl-functionalised MCM-41 (**5**)*

5 was prepared by the reaction of **3** and **4** with 2.2 equivalents in refluxing ethanol for 10 h. After cooling, **5** was collected by filtration, washed with ether and methanol. The sample was dried in vacuum (2 mm Hg) at 40 °C for 2 h.

2.5. Preparation of the chiral half unit of salen immobilized on MCM-41 (6)

6 was obtained by the condensation between **5** and the available chiral auxiliary (1S,2S)-(+)-1,2-diphenylethylenediamine or (1S,2S)-(+)-1,2-diaminocyclohexane with 2.2 equivalents in a refluxing ethanol solution for 14 h. After cooling, **6** was collected by filtration, washing with methylenechloride and methanol, and drying in vacuum at 40 °C.

2.6. Preparation of 2,4-di-tert-butylsalicylaldehyde (7)

2,4-di-*tert*-butylsalicylaldehyde **7** was synthesized by the reaction of 2,4-di-*tert*-butylphenol and paraformaldehyde in a refluxed anhydrous toluene according to the procedure reported by Casiraghi et al. [13]. 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 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 2 N HCl and extracted with diethyl ether. The ether extract was washed with a saturated NaCl solution, dried with $MgSO_4$ and concentrated to leave crude salicylaldehyde. 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.

2.7. Preparation of chiral (salen) Co(II) complexes immobilized on MCM-41 (8a)

8 was prepared by the reaction between 1.0 equivalent chiral half unit of salen immobilized on MCM-41 **6** and 2.0 equivalents salicylaldehyde derivatives (2,4-di-*tert*-butylsalicylaldehyde or salicylaldehyde) in a refluxing ethanol for 18 h. Then, the chiral salen Co(II) complex immobilized on MCM-41 was readily accomplished by refluxing an ethanolic solution of a salen ligand **8** with 2 equivalents of cobalt(II) acetate tetrahydrate in air for 2 h. The resulting mixture **8a** was filtered and washed several times with methylene chloride and methanol.

2.8. Preparation of the homogeneous unsymmetrical salen complexes (11)

10 mmol salicylaldehyde (or *o*-vanillin) 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 (or *o*-vanillin) took 5 h. A pale-yellow creamy solid **9**, namely chiral half unit [14], was obtained after evaporation of solvent under vacuum and washing with water to remove the unreacted diamines. 10 mmol of the chiral half unit **9** in 20 ml ethanol was added dropwise to the 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 **11** was collected by filtration and recrystallized from ethanol.[1]

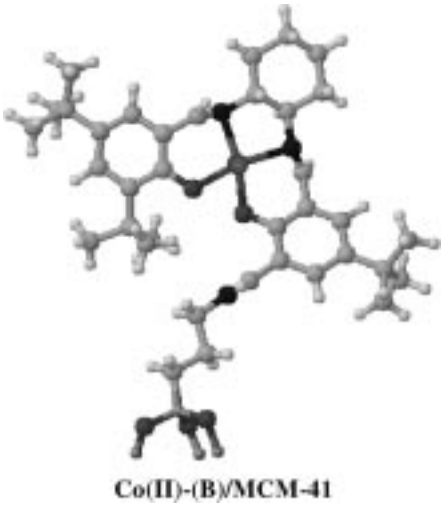
2.9. General procedure for the asymmetric catalytic reduction of ketones with sodium borohydride

The modification of $NaBH_4$ (0.75 mmol) with ethanol (0.75 mmol) and tetrahydrofurfuryl alcohol (5.15 mmol) in 5 ml of chloroform ($CHCl_3$) was performed for 3 h at 0 °C before the reaction. H_2 was released during the mixing. The pre-modified borohydride was added to the solution of ketone (0.25 mmol) and Co(II) complex catalyst (0.0175 mmol) in 5 ml of chloroform at −20 °C. The reaction mixture was stirred for 2 h at −20 °C. After finishing the reaction, the product was filtered and distilled from the mixture. The ee% values were determined by the capillary GC using chiral columns (CHORALDEX™, Gamma-cyclodextrin trifluoroacetyl, 40 m × 0.25 mm i.d. (Astec)).

3. Results and discussion

The structure of chiral salen ligands immobilized on MCM-41 is shown in figure 1. It reveals that the Co center adopts a near planar geometry with phenyl groups in the salicylaldehyde units. Frunza et al. [11] reported that the embedded chiral salen complex was probably parallel aligned to the wall of the mesopores in MCM-41, when the complexes were loaded in the pores by impregnation. The ligand plan in figure 1 may be almost perpendicular to the MCM-41 surfaces. The presence of bulky groups in Co(II)-(B)/MCM-41 prevents the substrate approach from the left side of the complex. The substituents on the diimine bridge could also lead to the more effective differentiation of substrate approaches. In the asymmetric borohydride reduction

[1] Sample D: $[a]_D^{20}$ +162.8 (c = 1.0, $CHCl_3$), IR (CCl_4): 2942, 2861, 1632, 1581, 1498, 1479, 1461, 1407, 1389, 1361, 1279, 1263, 1251, 1201, 1173, 1150, 1117, 1093, 1043, 1030, 974 cm^{-1}. ^{1}H-NMR ($CDCl_3$/TMS): 1.31 (s, 9 H), 1.45 (s, 9 H), 1.62–2.01 (m, 8 H), 2.44 (s, 2 H), 2.97 (m, 1 H), 3.43 (m, 1 H), 3.75 (q, 1 H), 4.08 (d, 1 H), 6.87 (t, 1 H), 7.03 (d, 1 H), 7.12–7.28 (m, 2 H), 7.35 (t, 1 H), 7.46 (d, 1 H), 8.40 (s, 2 H). ^{13}C-NMR ($CDCl_3$/TMS): 24.4, 29.8, 31.3, 33.1, 37.2, 72.4, 116.8, 118.4, 122.2, 124.8, 125.5, 126.7, 128.2, 131.3, 132.0, 132.2, 136.2, 160.8, 164.6, 165.7 ppm.
Sample E: $[a]_D^{20}$ +423.6 (c = 1.0, $CHCl_3$), IR (CCl_4): 2931, 2859, 1600, 1468, 1439, 1391, 1364, 1278, 1256, 1203, 1172, 1120, 1092, 1042, 1030, 973, 907 cm^{-1}. ^{1}H-NMR ($CDCl_3$/TMS): 1.19–1.40 (m, 21 H), 1.47–2.01 (m, 8 H), 3.29 (m, 2 H), 3.67 (q, 2 H), 3.85 (s, 2 H), 6.75 (m, 1 H), 6.98 (s, 1 H), 7.15–7.25 (m, 1 H), 7.30 (s, 1 H), 7.46 (d, 1 H), 8.30 (s, 2 H). ^{13}C-NMR ($CDCl_3$/TMS): 24.0, 29.4, 31.3, 33.9, 34.9, 55.7, 72.3, 113.7, 117.8, 123.0, 125.9, 136.2, 139.8, 157.9, 164.7, 165.7 ppm.



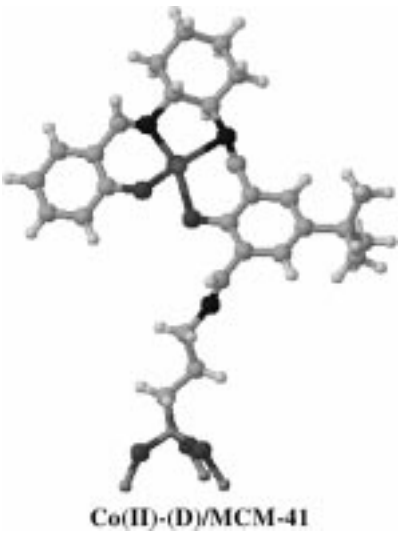


Figure 1. The structure of chiral salen complexes immobilized on MCM-41.

of ketones, the enantiofacial selection of corresponding (S)-alcohols to (S,S)-Co(II) chiral salen complexes is observed, and it can be explained by considering the favorable approaches of substrates through the open site. The optimal design of salen structure is important to improve the enantioselectivity.

The obtained MCM-41 showed a very intense (100) peak in the X-ray powder diffractogram and the calculated d_{100} spacing was 5.2 nm. The pore size distribution of MCM-41 synthesized by the rapid evaporation method in this work is shown in figure 2. The pore size determined by N_2 adsorption was 4.3 nm, as shown in figure 2. It has been reported that the difference between the pore size determined by N_2 adsorption and the intrinsic pore diameter may be about 1.0 nm [15]. Figure 3 shows the TEM image of purely siliceous MCM-41. The MCM-41 prepared in the acidic mixture by this modification method exhibited a fully disordered mesopore system. MCM-41 with disordered mesopores has been synthesized by Ryoo et al. [16] in alkaline media (pH = 10.2) using ethylenediaminetetraacetic acid tetrasodium salt. MCM-41 could be synthesized with a

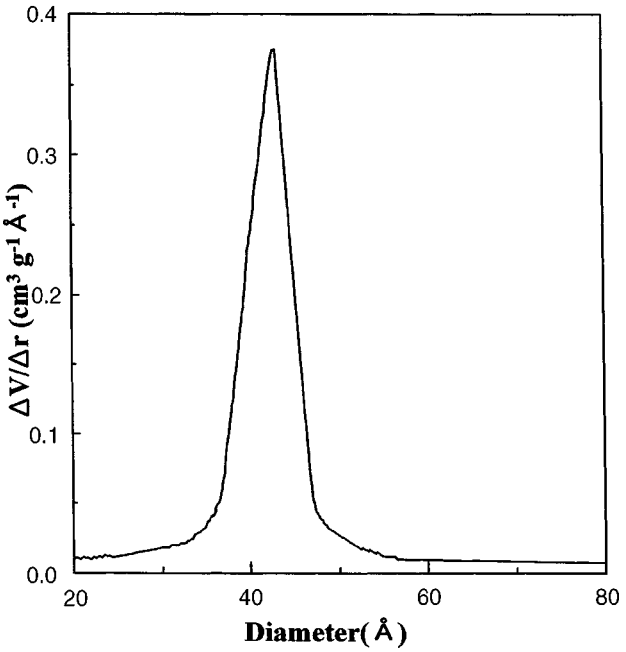


Figure 2. The pore size distribution of MCM-41 obtained by the evaporation method.

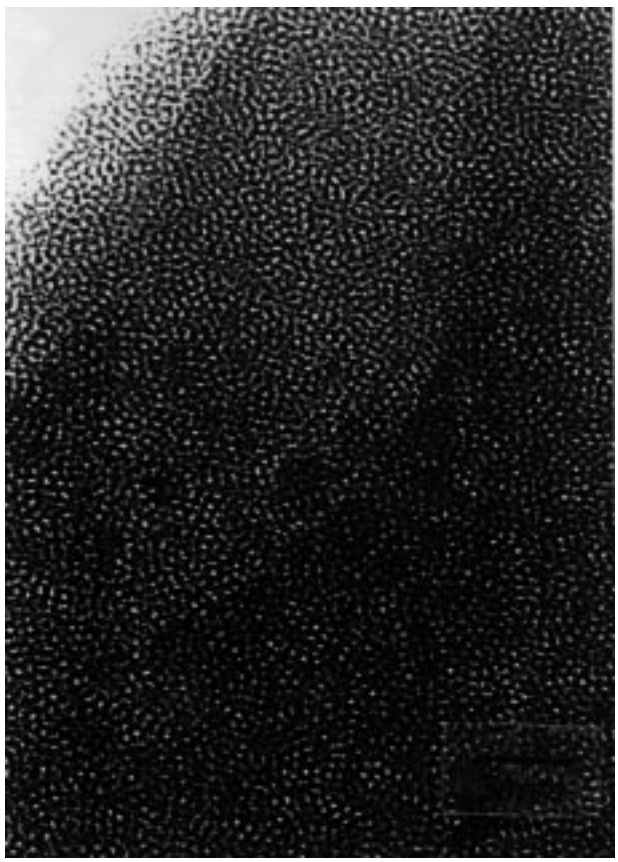


Figure 3. TEM image of MCM-41 used for immobilization of chiral salen complexes.

high crystallinity within 12 h by the evaporation method. This MCM-41 sample was used to immobilize the chiral salen complexes, as shown in scheme 1.

Figure 4 shows the FT-IR spectra of MCM-41, the homogeneous chiral salen complex and the salen ligand immobilized on MCM-41. In the IR spectra, both the homogeneous salen complex and the heterogenized one show the characteristic band at 1640 cm^{-1} and this peak is not found on the IR spectrum of pure MCM-41. The formation of a C=N bond in the salen complex can be characterized by this new band at 1640 cm^{-1}. In addition, to confirm that the organic species grafted on MCM-41 such as **8a** have the salen structure, sample **8a** was dissolved in HF solution and then the organic compound was extracted with CH_2Cl_2 solvent. After complete removal of the solvent, the organic compound was analysed by H-NMR. H-NMR characterization of the extract compound shows that the condensation of 3-*tert*-butyl-2,6-diformylphenol with diamines occurred. The H-NMR spectrum of the immobilized salen sample was the same as that of homogeneous salen ligand. The peaks at 6.5–8.8 ppm are due to the aromatic (=C–H) protons and those at 1.2–1.5 ppm assigned to the protons of terminal *tert*-butyl group. Then, the signals at 1.6–1.9 ppm are for the protons of CH_2 in cyclohexane. The bands at 3.3 and 4.4 ppm are assigned to the proton in the CHN bond and those at 7.2 and 7.6 ppm to that in CH=N, respectively, as reported by Tokunaga et al. [17]. The H-NMR spectra of the organic compound extracted from sample **8a** prove the formation and grafting of the chiral salen complex on MCM-41.

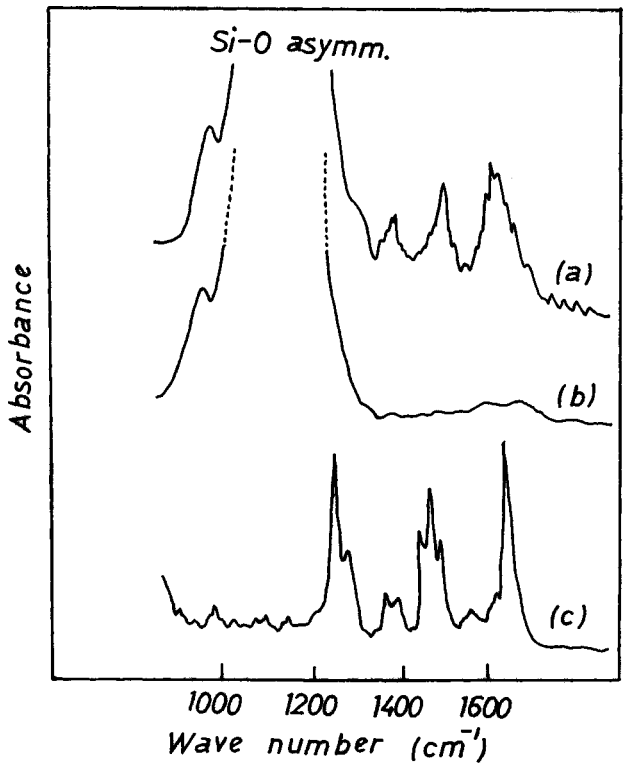
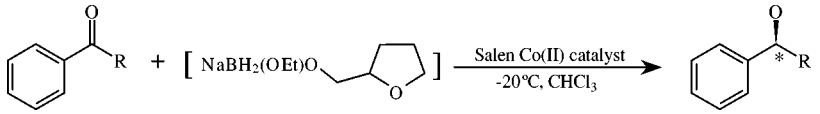


Figure 4. FT-IR spectra of (a) sample (**8**)-(A)/MCM-41, (b) pure MCM-41 and (c) chiral salen compex (A).

Various methods have been developed for the enantioselective reduction of ketones. Recently, Nagata et al. [18] reported that a set of ketones were asymmetrically reduced over the conventional chiral salen Co(II) complexes of symmetrical type with high ee%. In this case, the modification of $NaBH_4$ with tetrahydrofurfuryl alcohol (THFA)–ethanol or THFA–methanol was applied to the reduction of ketones.

The tendencies to reactivity and enantioselectivity of (salen) Co(II) complex immobilized on MCM-41 and the homogeneous catalyst were compared in the reduction of α-tetralone and acetophenone by sodium borohydride and alcohols. The obtained result is given in table 1. From the table, it can be seen that the unsymmetrical salen Co(II)-(D) and -(E) afford a more improved level of enantioselectivity

Table 1
Enantioselective borohydride reduction of ketone catalyzed by asymmetrical chiral Co(II) complexes.[a]

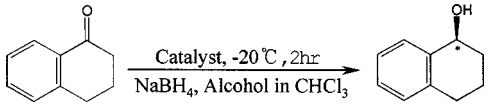


Entry	Substrate	Catalyst	Time (h)	ee[b] (%)	Conv. (%)
1	α-tetralone	Co(II)-(A)	1	17(S)	93
2	α-tetralone	Co(II)-(A)/MCM-41	2	25(S)	98
3	α-tetralone	Co(II)-(B)	1	16(R)	99
4	α-tetralone	Co(II)-(B)/MCM-41	2	23(R)	98
5	α-tetralone	Co(II)-(C)	1	22(S)	96
6	α-tetralone	Co(II)-(D)	1	65(S)	99
7	α-tetralone	Co(II)-(D)/MCM-41	2	73(S)	98
8	α-tetralone	Co(II)-(E)	1	46(S)	99
9	α-tetralone	Co(II)-(E)/MCM-41	2	53(S)	99
10	Acetophenone	Co(II)-(C)	1	15(S)	95
11	Acetophenone	Co(II)-(D)	1	31(S)	81
12	Acetophenone	Co(II)-(D)/MCM-41	2	38(S)	75

[a] Reaction conditions: substrate 0.25 mmol, Co(II) catalyst 0.0175 mmol, $NaBH_4$ 0.75 mmol, EtOH 0.75 mol, THFA 5.15 mmol; $NaBH_4$, tetrahydrofurfuryl alcohol (THFA) and ethanol (or methanol) were stirred for 3 h at 0 °C in 5.0 ml $CHCl_3$ solvent before reaction. The catalyst and the substrate were added to this pre-modified borohydride solution at −20 °C.

[b] The ee% values were determined by capillary GC using chiral columns.

Table 2
The effect of alcohol addition on the enantioselectivity in the asymmetric reduction of tetralone.



Entry	Catalyst	Catalyst (mol%)	Alcohol	ee (%)	Conv. (%)
1	Co(II)-(D)/MCM-41	10	None	15(S)	<10
2	Co(II)-(D)/MCM-41	10	EtOH	65(S)	60
3	Co(II)-(D)/MCM-41	10	THFA	68(S)	85
4	Co(II)-(D)/MCM-41	10	THFA + MeOH	75(S)	99
5	Co(II)-(D)/MCM-41	10	THFA + EtOH	75(S)	99

in the enantioselective borohydride reduction of aromatic ketones than the conventional symmetrical salen catalysts of Co(II)-(A) and -(B) among the homogeneous catalysts. The higher optical yield was obtained over the salen ligands synthesized from the 1,2-diaminocyclohexane derivative. Introduction of a methoxy group into the unsymmetrical salen ligands resulted in a decrease of enantioselectivity. The conventional Co(II)-(D), containing one bulky group at the *para* position to the salen oxygen, showed a selective catalytic activity for the reduction of α-tetralone. The catalysts Co(II)-(A) and -(B) having two *tert*-butyl groups resulted in a very low enantioselectivity. The presence of bulky groups to prevent the substrate approach is also crucial to the enantioselectivity in borohydride reduction of ketone. The catalysts having bulky groups near both salen oxygens such as Co(II)-(A) resulted in a lower enantioselectivity. Furthermore, the optically active Co(II) complexes of unsymmetrical salen catalyzed the reduction of aromatic ketones with sodium borohydride and the Co(II) chiral salen catalyst immobilized on MCM-41 exhibited a slightly higher enantiosectivity for reduction than the homogeneous complexes of the same structure, respectively. For this reaction, the modification of $NaBH_4$ with tetrahydrofurfuryl alcohol (THFA)–ethanol or THFA–methanol was applied to the reduction of acetophenones and α-tetralone, as reported by Nagata et al. [18]. It is noted that the proper selection of alcohol in the combination of THFA influenced the enantioselectivity, as indicated in table 2. Higher optical purity of 75% ee was obtained when the mixed solution of THFA and ethanol was used in the reduction of α-tetralone. The conversion and the enantioselectivity were very low without the addition of alcohol. The use of the ethanol–THFA combination resulted in an improvement of ee%. Homogeneous chiral salen Co(II) complexes and the prepared solid samples exhibited a dark red color. After using (salen) Co(II) complexes immobilized on MCM-41 as catalyst, the resultant solution exhibited no color and no Co was detected in the solution. Furthermore, the immobilized salen catalyst was heated to reflux in $CHCl_3$ solvent for 3 h and the extraction liquid was concentrated for H-NMR analysis. H-NMR spectra confirmed no chiral salen complexes exist in the extract. This means the (salen) Co(II) complexes immobilized on mesoporous materials are stable during the reaction and the salen ligands

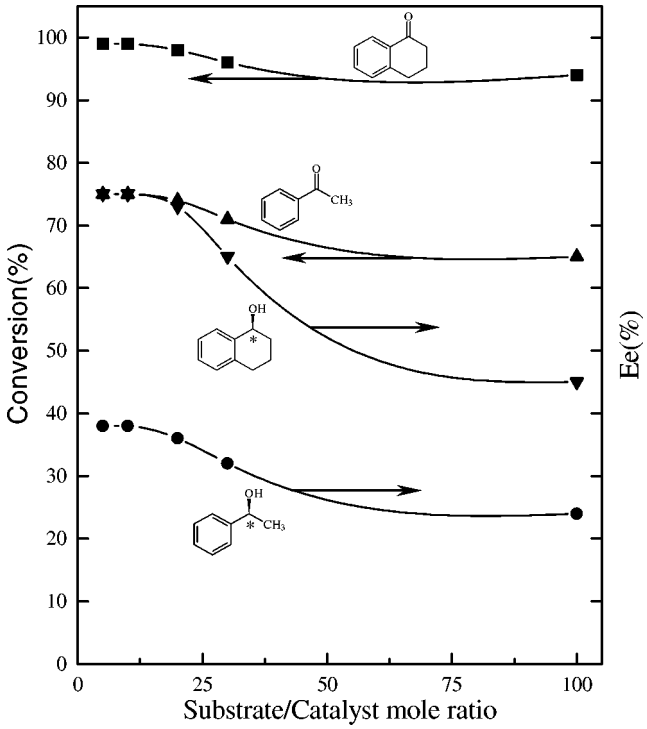


Figure 5. The effect of substrate/catalyst mole ratio on the conversion and the enantioselectivity in the reduction of α-tetralone and acetophenone on the Co(II)-(D)/MCM-41 catalyst.

exist in the pore system without any extraction. The catalytic activity and selectivity of salen Co(II) complexes immobilized on MCM-41 have not changed more or less after several times of reusing. The catalyst was reused after washing with CH_2Cl_2 solvent and drying under vacuum at 60 °C.

The effect of the amount of salen catalyst on the enantioselectivity of the borohydride reduction of ketone was investigated using the new unsymmetrical salen catalyst of Co(II) complexes. The results are summarized in figure 5. The asymmetric borohydride reduction using a combined solution of $NaBH_4$ with THFA and ethanol was rapid even at -20 °C. The ee% of the product alcohol increased with decreasing substrate/catalyst mole ratio. The racemic product was obtained only when the reaction was performed without the addition of a chiral 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].

4. Conclusion

The new chiral (salen) complexes immobilized on MCM-41 could be synthesized by multi-grafting. The asymmetric catalytic reduction using chiral (salen) complexes immobilized on MCM-41 can be applied with success and the unexpectedly high enantioselectivities are attainable in α-tetralone and acetophenone reduction. On the basis of asymmetric reduction results, the chiral (salen) complexes immobilized on a mesoporous material by the present procedure can be applied as effective asymmetric catalysts of the heterogeneous form. The catalysts prepared in this study may provide a rather unique approach to the asymmetric heterogeneous catalyst design.

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