

## Asymmetric Ring Opening of Terminal Epoxides Catalyzed by Chiral Co(III)-BF<sub>3</sub> Salen Complex Immobilized on SBA-16

Yong-Suk Kim, Choong-Young Lee,<sup>\*</sup> and Geon-Joong Kim<sup>\*</sup>

Department of Chemical Engineering, Inha University, Incheon 402-751, Korea. \*E-mail: kimgj@inha.ac.kr

Department of Chemical Environmental Technology, Inha Technical College, Incheon 402-752, Korea

Received April 10, 2009, Accepted June 25, 2009

The homogeneous BF<sub>3</sub> containing chiral Co(III) salen complexes were anchored non-covalently on the surfaces of mesoporous SBA-16 silica containing aluminum species. The Brønsted and Lewis acidic sites are attributed to the immobilization of fluorine functionalized chiral salen complexes on the supports. The FT-IR, UV, ESCA, and NMR analyses were performed to determine the structure of synthesized chiral salen catalysts. These heterogeneous catalysts could be applied in asymmetric ring opening of terminal epoxides by water and phenol derivatives. They showed very high enantioselectivity and yield more than 98% in the catalytic synthesis of optically active products.

**Key Words:** Asymmetric catalysis, Chiral cobalt salen, Non-covalent attachment, SBA-16, Mesoporous silica

### Introduction

Much effort has been devoted not only to the development of active heterogeneous catalyst but also to finding the ways to enable their repeated use. The heterogeneous catalysts have practical advantage in terms of catalyst separation, handling, and recycling ability without regeneration. Whereas some disadvantages such as a decrease in the selectivity can be happened by immobilization of the active homogeneous catalysts on the support. The synthesis of the mesoporous composites by various procedures have been studied widely to develop as a catalyst.<sup>1-4</sup> When compared with the microporous zeolites, mesoporous materials have larger size of pores and cages, which can provide the high probability for trapping the larger molecules such as salen complexes and more comfortable microenvironment for guest molecules.<sup>5,6</sup>

Several immobilization strategies have been shown to give stable and active heterogeneous catalysts.<sup>7-9</sup> It is well known that chiral cobalt salen complexes are very active and enantioselective in the asymmetric catalysis.<sup>10</sup> These salen-based catalysts are appealing candidates for covalent attachment of homogeneous chiral salen ligands to the inorganic supports, and the immobilized salen derivatives were shown to be efficient in organic reactions.<sup>11,12</sup> Our attention has been directed towards the development of heterogeneous chiral catalysts efficient for the kinetic resolution of terminal epoxides to obtain the optically pure products. From a practical synthetic point of view, phenol derivatives are appealing as an efficient candidate for nucleophiles in the ring opening of (±)epichlorohydrine (2-(chloromethyl)oxirane; ECH) providing direct access to enantiopure α-aryloxy alcohols using chiral cobalt-salen complexes.<sup>13,14</sup>

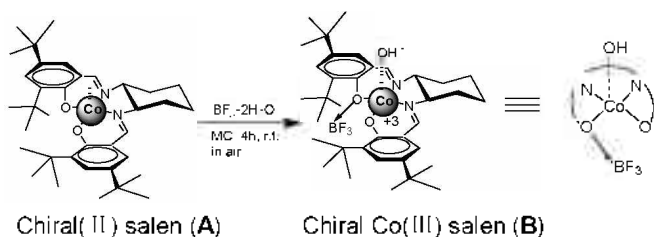
In this work, a method to anchor the active chiral cobalt (III) salen complexes by non-covalent bonding on the mesoporous SBA-16 support will be presented. The homogeneous BF<sub>3</sub>-containing chiral Co (salen) complexes were easily immobilized on the mesoporous supports by aluminium species through the electrostatic interactions. We have shown this

type chiral complexes immobilized over HF treated mesoporous MFI zeolite displayed the high enantioselectivity and reactivity for the asymmetric catalysis.<sup>15</sup> To the best of our knowledge, this immobilization method is so simple that it can provide facile route for anchoring the active sites in one step as compared to the covalent attachment which needs complicate synthetic procedures in the synthesis of various functionalized linkers. The obtained catalyst was tested in the asymmetric ring opening (ARO) of terminal epoxides by the nucleophiles such as water and phenol. They showed a high activity and selectivity in the enantioselective ring opening of terminal epoxides to synthesize valuable chiral intermediates such as beta-blockers.

### Experimental

**Synthesis of mesoporous SBA-16 support.** SBA-16 was prepared using poly(ethylene oxide)-block-poly(propylene oxide)-block-(ethylene oxide) as a structure directing agent (EO<sub>106</sub>PO<sub>70</sub>EO<sub>106</sub>, F127 (Aldrich)). The numbers in subscripts denote the molar ratios of each component in the block copolymer. In the typical synthesis of SBA-16, the block copolymer F127 (1 g) was dissolved in the mixed solution of distilled water (48 g) and concentrated hydrochloric acid (HCl, Fischer 35%, 2.1 g). After mixing for 30 min, *n*-butanol (3 g) and TEOS (Aldrich) were added into the system, and the mixture was prehydrolysed for 24 h at 45 °C with stirring. Then it was aged at 100 °C under the static condition for 24 h. The molar composition of each substrate for 1 g of copolymer (as a basis) was 1.0 TEOS; 0.041 *n*-BuOH; 0.020 HCl; 2.74 H<sub>2</sub>O. After the hydrothermal treatment, the precipitated solid was isolated by filtration and dried without any additional washing process at 100 °C for 24 h. The copolymer template was removed from the as-synthesized sample by calcination at 600 °C in air (heating rate; 1 °C/min).

**Chiral (Salen) cobalt complexes immobilized on mesoporous SBA-16.** AlCl<sub>3</sub>·6H<sub>2</sub>O was loaded on SBA-16 in the range of 10 ~ 30 wt% (Al basis), and the dried sample was calcined at



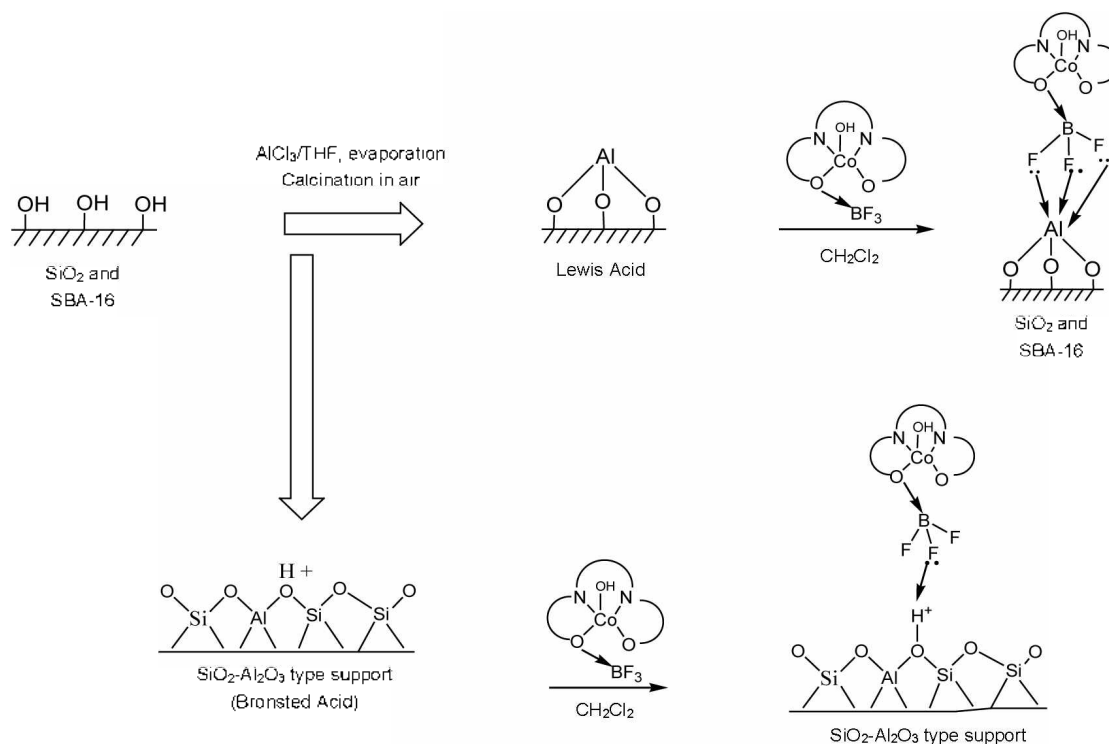
**Scheme 1.** Preparation of salen (Co)-BF<sub>3</sub> complex

550 °C. The chiral Co (salen) complex (**B**) was prepared by the same method as shown in the previous paper.<sup>15,16</sup> THF, CH<sub>2</sub>Cl<sub>2</sub>, hexane, cobalt (II) salen complex (**A**) and BF<sub>3</sub>·2H<sub>2</sub>O were purchased from Aldrich Co., and they were used without purification. The structures of parent cobalt (II) salen complex (**A**) and chiral Co(III)-BF<sub>3</sub>·OH salen (**B**) are indicated in Scheme 1. They will be denoted as Co(II)-(A) and Co(III)-(B) in this work, respectively. The Al-containing mesoporous SBA-16 was used as a support for immobilization of chiral (salen) cobalt complexes. The procedure to anchor the chiral complexes on the surfaces of mesoporous SBA-16 is shown in Scheme 2. Heterogenized chiral salen catalysts were prepared by refluxing Al-containing mesoporous SBA-16 with the solution containing chiral Co(III)-(B) in MC for 2 h. The powder sample in a dark green color was obtained by filtration and sequential washing with MC, THF and methanol until the filtrate was colorless. It was dried *in vacuo* to yield a heterogenized Co (salen) catalyst. In comparison, chiral Co(III)-(B) was attached on Al-containing SiO<sub>2</sub> gel (Fluka Chemicals: Kromasil 100-5-sil, pore volume

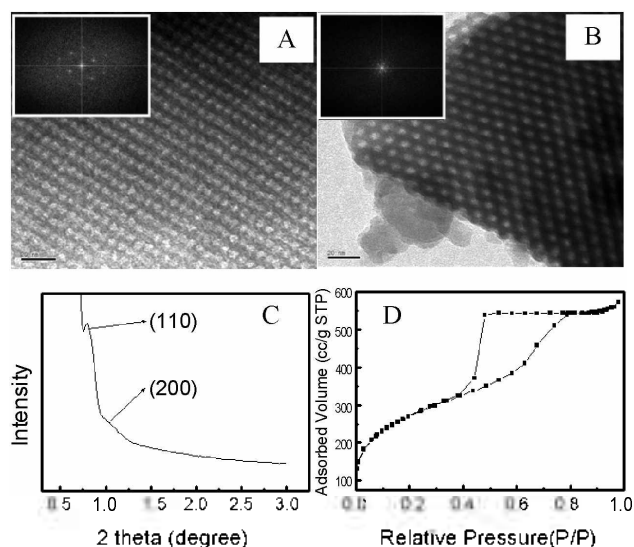
0.88 mL/g, BET surface area 305 m<sup>2</sup>/g by N<sub>2</sub> adsorption, particle size 6.1 μm) or pure SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support (Aldrich: silica-alumina catalyst support, Grade 135) by the same method as mentioned above to investigate the effect of pore structure on the catalytic activities.

**Characterization.** The phase structure of SBA-16 was determined by X-ray powder diffraction analysis (Phillips PW22XX and Rigaku DMAX 2500 diffractometer with CuKα radiation). The morphology and microstructures of samples were characterized by field emission transmission electron microscopy (FE-TEM, S-4200), porosity analyzer equipment (Micromeritics, ASAP 2010), and Al-MAS NMR spectroscopy (DSX 400 MHz Solid State Bruker NMR (at KBSI Daegu); 400 MHz with magic angle spinning at 10 kHz, π/2 pulse, 2 μs contact time, a repetition delay of 2 s and 30000 scans). FT-IR spectra were recorded on a BRUKER IFS 48 spectrometer. The anchored cobalt contents were determined by ICP-atomic emission spectroscopy (Optima 5300 DV, Perkin-Elmer (40 MHz, 1.5 K V RF-generator)).

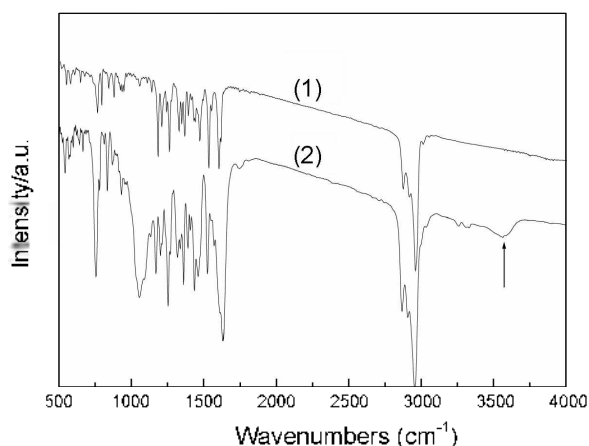
**General procedure for the catalytic reaction.** The catalytic activities were evaluated for the asymmetric ring opening of terminal racemic epoxides such as (±) ECH, propylene oxide (PO) and styrene oxide (SO) by water and phenol derivatives as nucleophiles. The reaction procedures were followed the same method reported previously.<sup>15</sup> The conversion of reactants and ee% (enantiomeric excess%) values of the ring opened product were determined by GC using a capillary chiral column (CHIRALDEX, γ-cyclodextrin trifluoroacetyl, 30 m × 0.25 mm i.d.) and by HPLC using a Chiralcel® OD-H column (24 cm × 0.46 cm).



**Scheme 2.** Schematic representation of heterogenized chiral (salen)-Co-BF<sub>3</sub>(B) on the solid support



**Figure 1.** (A) TEM images of (110) zone axes; (B) (100) zone of pore channel; (C) XRD pattern, and (D) N<sub>2</sub> isotherm for the calcined SBA-16 cubic mesoporous silica.



**Figure 2.** FT-IR spectra of chiral cobalt salen complexes in solution (1) Chiral (salen)-Co(II) complex(A); and (2) Chiral (salen)-Co(III)-BF<sub>3</sub>(B).

## Results and Discussion

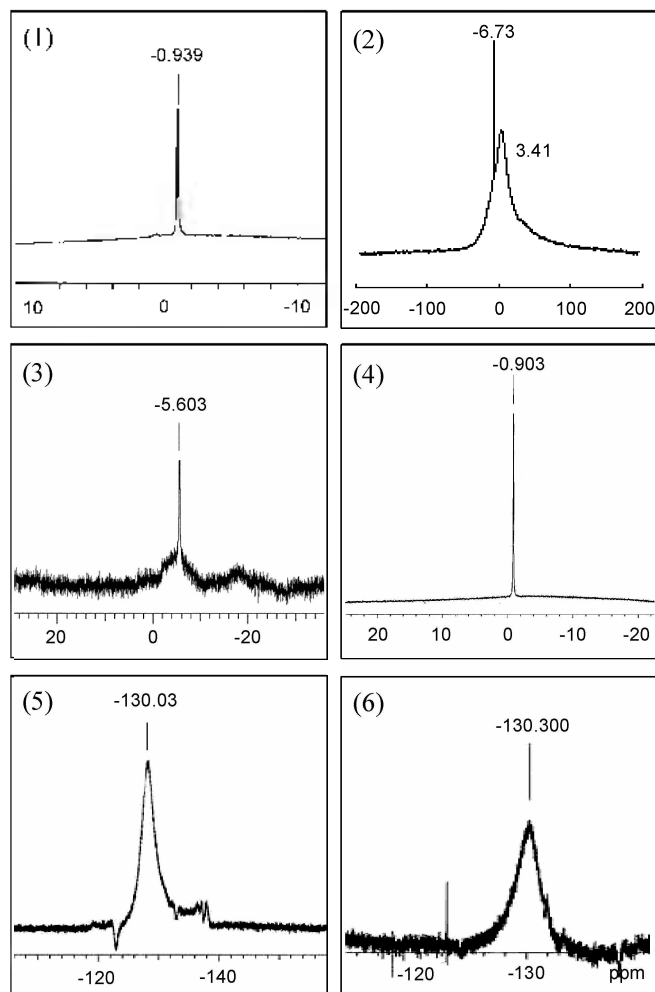
**Synthesis and characterization of SBA-16 support.** The mesoporous SBA-16 silica having 3-dimensional pore channels was synthesized as a support to immobilize the chiral salen complexes. X-ray diffraction analysis was carried out to investigate the structural feature of obtained SBA-16, and the result is presented in Fig. 1. Small angle X-ray powder diffraction for SBA-16 sample gave the peak patterns corresponding to a cubic ordering, as evidenced by the appearance of the (110), (200) and the (211) peaks. TEM images in Fig. 1, confirm the high mesoscopic ordering of SBA-16 synthesized in this work. The pore channels of SBA-16 appears to be arranged as a cubic lattice in the (110) direction. The regular hexagonal array of uniform channels was investigated with the (100) direction, showing the characteristic TEM images of SBA-16. For further characterization of the mesopore structure of SBA-16,

the nitrogen adsorption/desorption isotherm was determined. The N<sub>2</sub> isotherm of SBA-16 showed the increase in uptake of nitrogen and the change in the shapes of hysteresis loops extending from  $P/P_0 = 0.4 \sim 1.0$ , indicating the presence of mesopores. The steep closure of the hysteresis loop near  $P/P_0 = 0.4$  is representative for the ink-bottle shaped pores of SBA-16 material.

**Characterization of homogeneous salen complexes.** The homogeneous chiral Co(III)-(B) contains fluorine atoms as shown in Scheme 2. The homogenous catalyst (B) was synthesized first by the oxidation of Co(II) to Co(III) species in the presence of BF<sub>3</sub>·2H<sub>2</sub>O under the aerobic condition (Scheme 1). UV, FT-IR, ESCA, and NMR, analyses have been performed to determine the structure of synthesized Co(III)-(B). From the spectra of ESCA, it was clear that the structural change of cobalt salen was created after reaction between BF<sub>3</sub>·2H<sub>2</sub>O and Co(II)-(A), as reported previously.<sup>15,16</sup> For chiral Co(III)-(B), the increased oxidation state of cobalt (Co<sup>3+</sup>) was confirmed by ESCA analysis as compared to the starting Co<sup>2+</sup> in the salen complex after treatment of BF<sub>3</sub>·2H<sub>2</sub>O, using the Co<sup>III</sup>-OAc *Jacobsen* catalyst and Co(II)-(A) as reference samples. The binding energies of O<sub>1s</sub> did not vary between chiral Co(II)-(A) and *Jacobsen*-type catalyst [Co<sup>III</sup>-OAc]. Thus, the change in binding energy (O<sub>1s</sub>) of Co(III)-(B) is attributed to the coordination of boron species to the oxygen atoms in the salen complex by the Lewis-acid interaction. On the UV-Vis spectra, the solution of chiral Co(II) salen(A) showed the characteristic absorption bands near 360 nm and 430 nm in the spectra. But for the salen Co(III)-(B), the characteristic absorption band of Co(II)-(A) at 430 nm was disappeared, and the new band near 360 nm was appeared on the UV-Vis spectra. In comparison, the *Jacobsen* catalyst (III) also showed the characteristic absorption bands near 360 nm due to Co(III) oxidation state.

Furthermore, the homogeneous chiral Co(III)-(B) exhibited the absorption peak for hydroxyl group over 3600 cm<sup>-1</sup> on FT-IR spectra as shown in Fig. 2. Whereas OH groups were not found for the sample of Co(II)-(A). Those samples were dried sufficiently under the vacuum and heating.

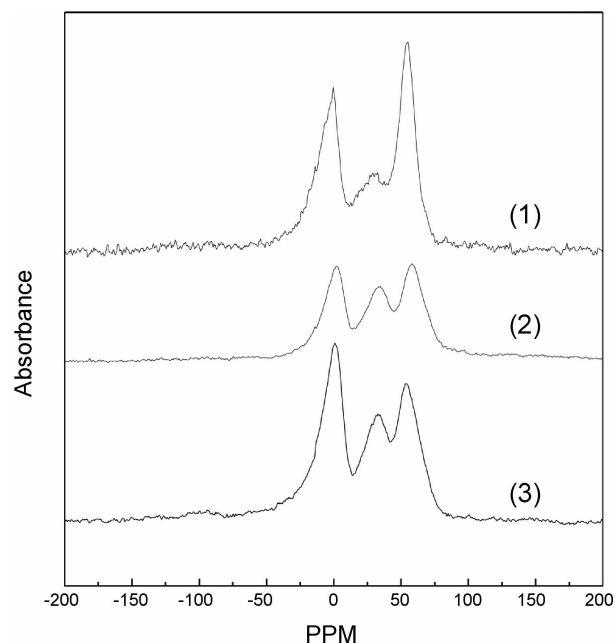
To analyze and identify the further structural characteristics of Co(III)-(B), <sup>11</sup>B and <sup>19</sup>F-NMR spectra for BF<sub>3</sub>·2H<sub>2</sub>O, BF<sub>3</sub>·Et<sub>2</sub>O, BF<sub>4</sub><sup>-</sup> (as ferroceniumtetrafluoroborate) sources and Co(III)-(B) were determined, respectively, and the results are shown in Fig. 3. Additionally the B-NMR spectrum of BF<sub>4</sub><sup>-</sup> ion-containing Co(III)-(B) was also determined. It is clear that the shift in peak position was observed due to the different environment in the boron sources. For BF<sub>3</sub>·2H<sub>2</sub>O (Fig. 3(1)), BF<sub>4</sub><sup>-</sup> source (Fig. 3(2)) and BF<sub>4</sub><sup>-</sup> ion-containing Co(III)-(B) (Fig. 3(3)), the characteristic peaks on the B-NMR spectra were observed at -0.939 ppm, 3.410 ppm (with additional -6.73 ppm) and -5.603 ppm, respectively. However, the boron species in Co(III)-(B) showed the peak at -0.903 ppm, indicating not the presence of boron anions but the same Lewis acidic interaction of boron like in the case of sample (Fig. 3(4)). On the F-NMR spectra for BF<sub>3</sub>·2H<sub>2</sub>O and Co(III)-(B), almost the same peak position was found at 130.03 and 130.30 ppm as shown in the spectra (5) and (6), respectively. It is well known that BF<sub>3</sub>·2H<sub>2</sub>O compounds exist as BF<sub>3</sub>OH<sup>(-)</sup> and H<sub>3</sub>O<sup>(+)</sup> ions in the solution.<sup>17</sup> Thus, there is a possibility of ionic pair formation between the cationic Co(·3) salen and anionic BF<sub>3</sub>OI<sup>(-)</sup> like *Jacobsen*-



**Figure 3.** The  $^{11}\text{B}$  NMR spectra of (1)  $\text{BF}_3 \cdot 2\text{H}_2\text{O}$ ; (2)  $\text{BF}_3 \cdot 1$  source (as ferroceniumtetrafluoroborate); (3)  $\text{Co(III)}$  salen complex synthesized using ferroceniumtetrafluoroborate (containing  $\text{BF}_4^-$  anion); (4)  $\text{Co(III)}$   $\text{BF}_3$  salen(**B**) (synthesized using  $\text{BF}_3 \cdot 2\text{H}_2\text{O}$ ); and  $^{19}\text{F}$  NMR spectra of (5)  $\text{BF}_3 \cdot 2\text{H}_2\text{O}$ ; and (6)  $\text{Co(III)}$  salen(**B**) having  $\text{BF}_3$  (synthesized from  $\text{BF}_3 \cdot 2\text{H}_2\text{O}$ ).

type catalyst ( $\text{Co}^{\text{III}}\text{-OAc}$ ) after treatment of cobalt(II)-(A) with  $\text{BF}_3 \cdot 2\text{H}_2\text{O}$ . From the results obtained in this work,  $\text{Co(III)-(B)}$  has formed no anionic boron species like  $\text{BF}_3\text{OH}^{(-)}$ , and then the 3 fluorines are present as a original state without the change in the properties. As a result, the analytical data for  $\text{Co(III)-(B)}$  led to a proposed structure of -3 oxidation state cobalt salen complex containing  $\text{BF}_3$  and OH units as depicted in Scheme 1.

**Immobilization of homogeneous salen complexes.** The  $\text{Co(III)-(B)}$  having  $\text{BF}_3$  group were easily attached onto the hydronium ions such as Brønsted acidic solids. For instance,  $\text{SiO}_2\text{-Al}_2\text{O}_3$  support having Brønsted acid sites mainly could immobilize the  $\text{Co(III)-(B)}$  in a large amount. They were adhered strongly to the solid surfaces even after washing with various polar solvents. We believe this unique immobilization is due to the adsorption of the complex on to the acidic sites ( $\text{H}^+$ ) of support through the hydrogen-bonding. However, the adsorption of  $\text{Co(III)-(B)}$  on the Lewis acid sites of aluminum present on the support can not be ruled out as indicated in

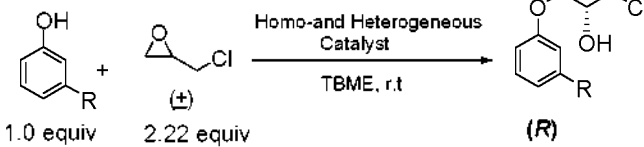


**Figure 4.**  $^{27}\text{Al}$  MAS NMR spectra of (1) 10 wt%  $\text{AlCl}_3$  loaded SBA-16 (calcined at  $550^\circ\text{C}$ ); (2) 30%  $\text{AlCl}_3$  loaded SBA-16 (calcined at  $550^\circ\text{C}$ ); (3)  $\text{Co(III)}$  salen(**B**)-anchored on the sample (2).

Scheme 2, since  $\text{Co(III)-(B)}$  were also attached strongly to the surfaces of pure  $\text{Al}_2\text{O}_3$ . They were not anchored on the pure  $\text{SiO}_2$ .

To perform the incorporation of aluminum ions into the framework,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  was impregnated on SBA-16 in the range of 10 ~ 30 wt%, and the dried sample was calcined at  $550^\circ\text{C}$ . There are many vacant tetrahedral sites and OH silanol groups on the surfaces of SBA-16 silica. In general, the silanol nest present on the surfaces of SBA-16 can be combined with aluminium species to form the tetrahedral sites (Brønsted acid) or octahedral sites (Lewis acidity). Yoon *et al.* have applied the impregnation method of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  to generate the acidic sites on the mesoporous silica.<sup>18</sup> In this work,  $^{27}\text{Al}$ -MAS-NMR analysis was performed to distinguish the coordination state of aluminium compound which were formed after Al loading on the supports and calcination in air.

Fig. 4 shows the  $^{27}\text{Al}$ -MAS-NMR spectra of Al-incorporated SBA-16 samples with the different loading amount. There are two distinct peaks with one small peak on the  $^{27}\text{Al}$ -MAS-NMR spectra of 10 wt%  $\text{AlCl}_3$ -loaded SBA-16 sample (Fig. 4(1)): The strong peak at the chemical shift of 60 ppm is related to the framework aluminium atoms with tetrahedral coordination, and that peak at 0 ppm can be attributed to the non-framework aluminium (octahedral coordination).<sup>19</sup> When 30 wt% of  $\text{AlCl}_3$  was impregnated on the mesoporous SBA-16 and calcined at  $550^\circ\text{C}$ , three distinct peaks on the  $^{27}\text{Al}$ -MAS-NMR spectra were found as in Fig. 4(2). The peak at chemical shift of 20 ppm in the spectrum is interpreted as 5-coordinated Al site: namely these aluminums are surrounded by 4 oxygens in the framework with one adsorbed molecule such as water at the non-framework position.<sup>19</sup> However, the portion of 5- and 6-coordinated sites have increased as compared to the tetrahedral sites in the framework, with increased loading amount of  $\text{AlCl}_3$ .

**Table 1.** Asymmetric ring opening of ( $\pm$ )-ECH with various phenols catalyzed by homo- and heterogeneous chiral Co(III) salen catalysts


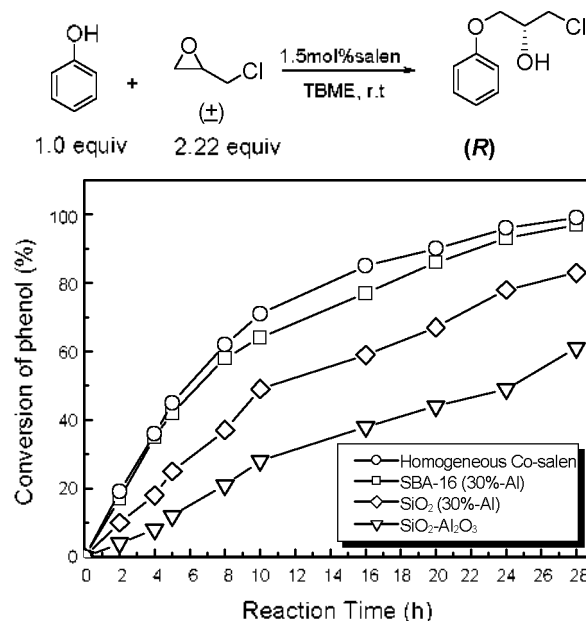
Sr.No	Substrate(R)	Catalyst <sup>d</sup>	Yield (%) <sup>c</sup>	%ee <sup>b</sup>
1	H	Homogeneous ( <b>B</b> )	86	> 98
2	CH <sub>3</sub>	Homogeneous ( <b>B</b> )	73	97
3	Cl	Homogeneous ( <b>B</b> )	74	> 98
4	H	Al(10%)-SiO <sub>2</sub> -( <b>B</b> )	60	97
5	H	Al(20%)-SiO <sub>2</sub> -( <b>B</b> )	65	98
6	H	Al(30%)-SiO <sub>2</sub> -( <b>B</b> )	72	98
7	H	SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> -( <b>B</b> ) <sup>e</sup>	52	91
8	Cl	Al(30%)-SiO <sub>2</sub> -( <b>B</b> )	75	95
9	CH <sub>3</sub>	Al(30%)-SiO <sub>2</sub> -( <b>B</b> )	78	98
10	H	Al(20%)-SBA-16-( <b>B</b> )	81	98
11	H	Al(30%)-SBA-16-( <b>B</b> )	88	> 98
12	CH <sub>3</sub>	Al(30%)-SBA-16-( <b>B</b> )	70	> 98
13	Cl	Al(30%)-SBA-16-( <b>B</b> )	73	98

Reaction time; 28 h. <sup>a</sup>Isolated yield based on the mole of reactant phenol. <sup>b</sup>% ee was determined by chiral HPLC and chiral GC. <sup>c</sup>SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> was purchased from Aldrich Co. <sup>d</sup>Catalyst loading was fixed as 1.5 mol% based on Co-salen relative to phenol. The catalyst Al(30%)-SBA-16-(**B**) means that Co-salen complex(**B**) was immobilized on 30 wt% aluminum chloride-loaded SBA-16 support. In all cases, Co-salen complex(**B**) was used for immobilization.

on the support (Fig. 4(2)). Fig. 4(3) shows the <sup>27</sup>Al-MAS-NMR spectrum of Al(30%)-SBA-16-(**B**) sample. This catalyst denotes the Co(III) salen complex(**B**) immobilized on 30 wt% AlCl<sub>3</sub>-loaded SBA-16. After attachment of Co(III)-(B), it was found that the relative peak intensity at 0 ppm has increased as compared to that at 20 or 60 ppm, indicating the number of 6-coordination of Al was increased. As shown in Scheme 2, Co(III)-(B) can be easily adhered onto the Brønsted acid sites in tetrahedral position, but the attachment of this type would not change the coordination of Al species. Thus, the increase of 6-coordinated Al on the <sup>27</sup>Al-MAS-NMR spectrum can be interpreted as an immobilization of Co(III)-(B) on Lewis acidic site which was formed by the non-framework Al species.

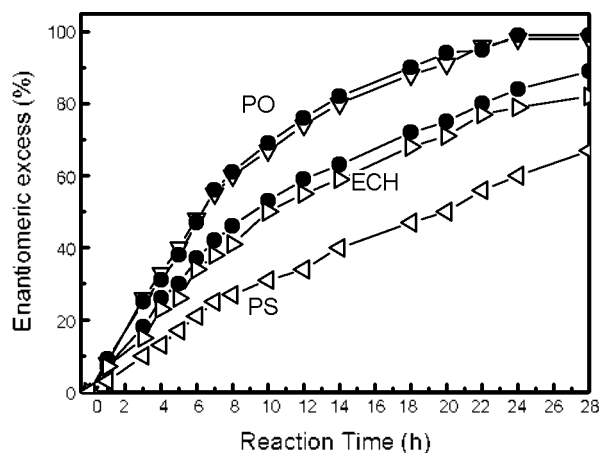
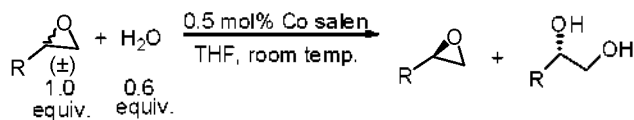
The SBA-16 can supply the vacant spaces enough to introduce the very big (salen) complexes inside the pore channels. The characteristic IR peaks for homogeneous salen appeared at the position of 2958 ~ 2950, 1612 and 1535 cm<sup>-1</sup> on the spectra. However, the chiral Co(III)-(B)-anchored mesoporous SBA-16 has exhibited the similar absorption bands of the pure homogeneous chiral (salen) complex. This result indicates that the chiral Co(III)-(B) was successfully attached to Al-containing SBA-16.

**Catalytic activity in asymmetric synthesis.** In Table 1, the activities of heterogeneous catalysts are summarized after examination for the ARO of racemic epoxides by phenol derivatives. It is evident that the immobilized Co(III)-(B) on SBA-16 exhibited a high activity relative to the homogeneous one. As shown in Table 1, ARO reaction was applicable for the synthesis of enantiopure phenoxy compounds by using 3

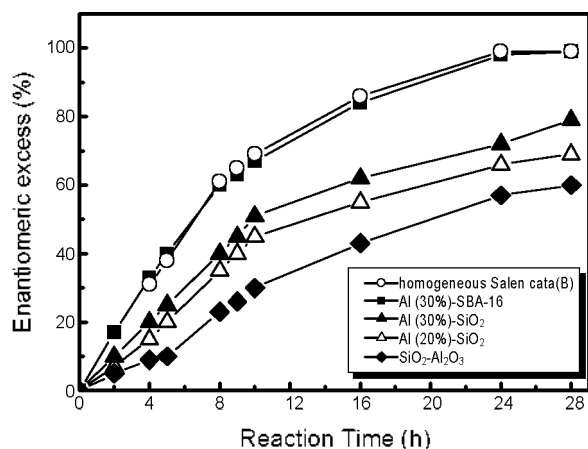
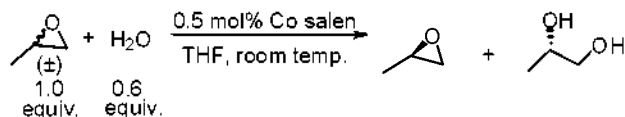
**Figure 5.** The catalytic activity of heterogeneous catalysts in the ring opening of ( $\pm$ )-ECH with phenol. (For SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst, Co-salen complex(**B**) was anchored without loading of AlCl<sub>3</sub> on the support.)

kinds of phenol derivatives to resolve ( $\pm$ )-ECH as nucleophiles. Overall, the kinetic resolutions of ( $\pm$ )-ECH by phenol, chlorophenol and cresol in the presence of salen catalysts were proceeded in efficient manner, affording corresponding  $\alpha$ -aryloxy alcohols in a high yield with excellent enantioselectivity up to 98% ee.

To observe the trends in the activity and enantioselectivity of chiral cobalt-salen complexes immobilized on Al-containing porous supports as well as on the acidic SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, the reactivities of the homogeneous and heterogenized chiral Co(III)-(B) were examined in the kinetic resolution of ( $\pm$ )-ECH with phenol with a prolonged reaction time. Fig. 5 shows that ARO of terminal epoxides was opened enantioselectively by phenol in the presence of heterogenized chiral Co(III) salen complexes. When the Co(III)-(B)/SBA-16 was used as a catalyst, the reaction proceeded smoothly at room temperature and provided a high enantioselectivity. The Al(30%)-SBA-16-(B) exhibited the almost same catalytic activities relative to the homogeneous Co(III)-(B) as can be seen in Fig. 5. In comparison, pure macroporous SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support was used to anchor the same type of salen complexes. However, with the chiral Co(III)-(B)/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst, a lower catalytic activity was obtained even after the prolonged reaction time. The low enantioselectivity of the Co(III)-(B)/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst is attributed to the presence of strong acid sites remaining on the surfaces of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>. The Brønsted acidity was found to open the epoxide ring achi- rally in the presence of water. The heterogenized Co(III)-(B) on the 30% Al-loaded SiO<sub>2</sub> gel exhibited the lower activity than those immobilized on the mesoporous SBA-16 under the same amount loading of salens. This result indicates that three dimensional mesoporosity of supports gave an important role in the catalysis. The mesoporosity may provide the high probability that any salen catalyst in the pore can interact with



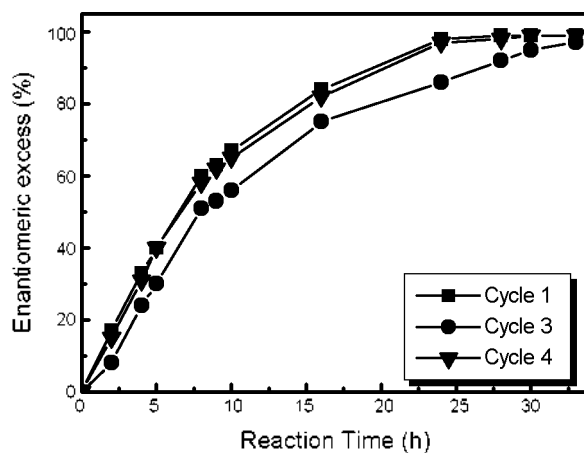
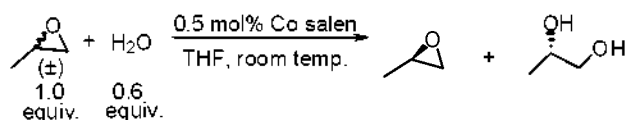
**Figure 6.** The activity of various catalysts in the HKR of (±)-terminal epoxides. (●: Homogeneous Co-Salen catalyst (B); ▽, >, ◁: Heterogeneous Al(30%)-SBA-16-(B) catalyst.).



**Figure 7.** The catalytic activity of heterogeneous catalysts in the HKR of (±)-PO.

other catalyst.

The reactivity and enantioselectivity of the homogeneous and heterogenized chiral Co(III)-(B) were examined in the hydrolytic kinetic resolution (HKR) of (±)-ECH, PO and SO with water, and the results are summarized in Fig. 6. This figure shows that ARO reaction of terminal epoxides was catalyzed enantioselectively by the heterogenized chiral Co(III)-(B). The reaction was performed efficiently at room temperature, providing a high selectivity up to 98% ee in good yield. The Al(30%)-SBA-16-(B) catalysts exhibited almost the same catalytic activities relative to the homogeneous Co(III)-(B) in the HKR of ECH and PO, respectively.



**Figure 8.** The recyclability of heterogeneous chiral Al(30%)-SBA-16-(B) in the kinetic resolution of (±)-PO with water. (In the case of cycle 4, the homogeneous salen complex (B) was attached on the used catalyst for regeneration. Cycle 3: without regeneration).

In Fig. 7, Al(30%)-SBA-16-(B) catalyst was identified as the most active and enantioselective among the applied catalysts. It is remarkable that Al(30%)-SBA-16-(B) is much more active as compared to catalyst SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-(B) and Al(30%)-SiO<sub>2</sub>-(B). As similar as in ARO reactions by phenol as mentioned previously, the results obtained in HKR of ECH also indicate that, both the ordered mesoporous structure and the high loading of active salen sites are essential for promoting the reaction.

Recyclability of chiral Co(III) salen complexes anchored on the mesoporous SBA-16 was investigated in the same reactions as mentioned above. The catalyst was collected by simple washing with MC, THF solvent for reuse after completion of reaction. The catalyst could be recycled efficiently, as summarized in Fig. 8. After three times reuse, heterogenized salen catalysts retained the high activity, but a decrease in enantioselectivity was found, indicating the slight extraction of salen complex from the support. The activity could be recovered after reattachment of homogeneous complexes on the reused catalysts, as shown in Fig. 8.

## Conclusion

The chiral salen cobalt(III) complexes were easily attached non-covalently on the surfaces of mesoporous SBA-16 silica containing aluminum species. The acidic sites generated by Al after calcination were attributed to the immobilization of fluorine functionalized chiral salen complexes on the supports. The structure of attaching chiral salen complexes were determined by instrumental analyses. The new heterogeneous catalysts showed high activity and enantioselectivity in the ARO of terminal epoxides by nucleophiles. Optically active terminal epoxides and  $\alpha$ -aryloxy alcohol compounds with up to 98% ee were obtained in high yield. Further studies to im-

prove the activity of heterogeneous catalysts for the asymmetric catalysis are currently underway.

**Acknowledgments.** This research was supported by Research grant of Inha Technical College in 2008.

### Reference

1. Karlsson, A.; Stöcker, M.; Schmidt, R. *Micropor. Mesopor. Mater.* **1999**, *27*, 181.
2. Demel, J.; Park, S.-E.; Cejka, J.; Stepanicka, P. *Catal. Today* **2008**, *132*, 63.
3. Nur, H.; Hamid, H.; Endud, S.; Hamdan, H.; Ramli, Z. *Mater. Chem. Phys.* **2006**, *96*, 337.
4. Kim, J. M.; Kwak, J. H.; Jun, S.; Ryoo, R. *J. Phys. Chem.* **1995**, *99*, 16742.
5. Groen, J. C.; Bach, T.; Ziese, U.; Paulaime-van Donk, A. M.; De Jong, K. P.; Moulijn, J. A.; Perez-Ramirez, J. *J. Am. Chem. Soc.* **2007**, *127*, 10792.
6. Cejka, J.; Mintova, S. *J. Catal. Rev.* **2008**, *49*, 457.
7. Yang, H.; Li, J.; Yang, J.; Liu, Z.; Yang, Q.; Li, C. *Chem. Commun.* **2007**, 1086.
8. Seebach, D.; Marti, R. E.; Hintermann, T. *Helv. Chim. Acta* **1996**, *79*, 1710.
9. Vasylev, M. V.; Neumann, R. *J. Am. Chem. Soc.* **2004**, *126*, 126.
10. Tokunaga, M.; Larrow, J. F.; Kakiuchi, F.; Jacobsen, E. N. *Science* **1997**, *277*, 936.
11. Schaus, S. E.; Brandes, B. D.; Larrow, J. F.; Tokunaga, M.; Hansen, K. B.; Gould, A. E.; Furrow, M. E.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2002**, *124*, 307.
12. Thakur, S. S.; Chen, S.-W.; Li, W.; Shin, C.-K.; Kim, S.-J.; Koo, Y. M.; Kim, G.-J. *J. Organomet. Chem.* **2006**, *691*, 1862.
13. Ready, J. M.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1999**, *121*, 6086.
14. Ready, J. M.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2001**, *123*, 2687.
15. Lee, K.-W.; Lee, C.-Y.; Kawthekar, R. B.; Kim, G.-J. *Bull. Korean Chem. Soc.* **2009**, *30*, 389.
16. Lee, K.-W.; Kawthekar, R. B.; Kim, G.-J. *J. Korean Ind. Eng. Chem.* **2007**, *18*, 330.
17. Greenwood, N. N.; Thomas, B. S. In *Comprehensive Inorganic Chemistry* (The Chemistry of Boron); Pergamon Press: Oxford, 1975; Chap. 11.
18. Yoon, S. B.; Sohn, K.; Kim, J. Y.; Shin, C.-H.; Hyeon, T. *Adv. Mater.* **2002**, *14*, 19.
19. Gan, J.; Wang, T.; Liu, Z.; Tan, W. *Stud. Surf. Sci. Catal.* **2007**, *170B*, 1567.