

Synthesis of New Bimetallic Chiral Salen Catalyst Bearing Co(BF₄)₂ Salt and Its Application in Asymmetric Ring Opening of Epoxide

Yong-Suk Kim, Choong-Young Lee,[†] and Geon-Joong Kim*

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

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The newly synthesized homogeneous chiral Co(III) salen complexes were anchored non-covalently on the acidic sites of mesoporous Al-SBA-15. The Bronsted and Lewis acidic sites are attributed to the immobilization of fluorine functionalized chiral salen complexes on the supports. XRD, BET, TEM, FT-IR and ESCA (XPS) analyses were performed to characterize the property of support, and the structure of new homogeneous and heterogeneous chiral Co salen catalyst. The homogeneous and heterogeneous catalysts could be applied in asymmetric ring opening of epichlorohydrin (ECH) by water. They showed very high enantioselectivity and a good yield up to 99% in the catalytic synthesis of optically active products.

Key Words: Asymmetric catalysis, Co(BF₄)₂ containing chiral salen, Non-covalent attachment, Mesoporous carbon

Introduction

Much effort has been devoted to development of active heterogeneous catalyst having practical advantages in terms of product separation and recycling. Whereas some disadvantages such as decrease in the selectivity may happen through anchoring the active homogeneous catalysts on the support. The synthesis of mesoporous composites has been studied widely to exploit the new type of catalysts.¹⁻⁴ Several immobilization strategies have been adopted to give stable and active heterogeneous catalysts.⁵⁻⁷ Since the chiral cobalt salen complexes are known to be very active and enantioselective in the asymmetric catalysis,⁸ they are appealing as excellent candidates for covalent attachment of homogeneous complexes to the inorganic supports. In this category, our attention has been directed towards the design and synthesis of new efficient chiral bimetallic catalysts based on the salen structure. In the previous our study, the dimeric or dinuclear salen complexes have shown the excellent activity in the asymmetric kinetic resolution (AKR) of terminal epoxides.⁹ Recently we have isolated the new salen catalysts containing transition metals salts, such as CoCl₂, Co(NO₃)₂, FeCl₂, NiCl₂, in the ligand structure.^{10,11} Their catalytic activity and enantioselectivity were dependent on the type of metal salts combined to the salen complexes in AKR reactions. Such types of bimetallic catalysts are remarkably efficient in the catalysis, showing two different metal sites to enhance the reactivity by synergy effect.¹¹

In addition, a method to anchor the active chiral cobalt salen complexes by non-covalent bonding on the support has been introduced.^{11,12} The homogeneous BF₃-containing salen was easily anchored on the mesoporous support by aluminum species through the electrostatic interaction after loading of AlCl₃.¹² The acidic sites generated by Al after calcination were attributed to the immobilization of fluorine functionalized chiral salen complexes on the supports.^{13,14} To the best of our knowledge, this non-covalent immobilization method is so simple

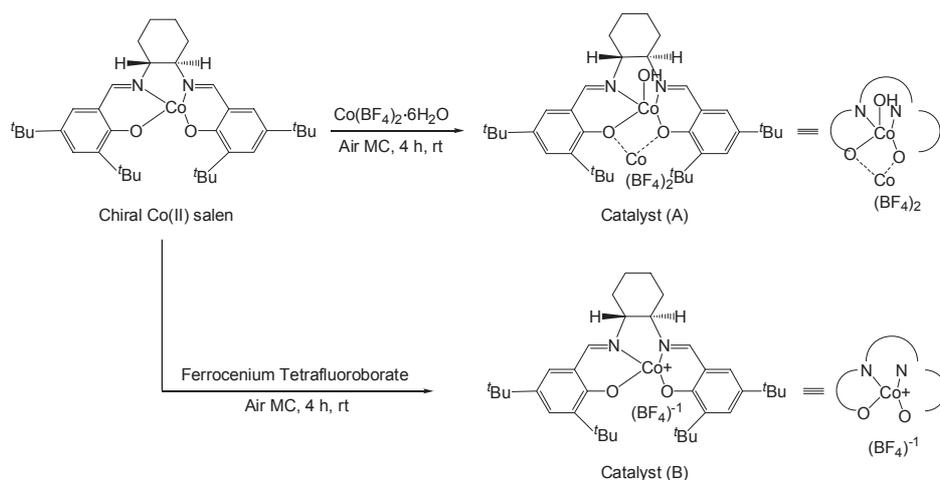
that it can provide facile route for anchoring the active sites in one step as compared to the covalent attachment which needs complicate synthetic procedures in the functionalized linker synthesis.

On the basis of such facts, the chiral cobalt salen complexes containing Co(BF₄)₂ salt were synthesized newly in current study. Their structure was determined by the instrumental analysis, and the catalytic activity has been examined for AKR reaction. The chiral salen complex of this type has never been exploited as a catalyst. However, it showed very high activity with a remarkable enantioselectivity in the asymmetric catalysis. We herein report that newly synthesized chiral cobalt (III) salen complexes were easily immobilized on the mesoporous supports through the electrostatic interactions on the acidic sites of mesoporous SBA-15 non-covalently. Furthermore, because this new catalyst contains two different cobalt sites, the drawback of activity decrease after immobilization of salens on the supports could be overcome through the activation of reactants by intramolecular catalysis. They showed very high activity and enantioselectivity in AKR for repeated use.

Experimental

Synthesis of mesoporous Al-SBA-15 support and its reverse replica of carbon. The Al containing Al-SBA-15 was synthesized from the pre-hydrolyzed silica and alumina sol using poly(ethylene oxide)-block-poly(propylene oxide)-block-(ethylene oxide) as a structure directing agent (EO₂₀ PO₇₀ EO₂₀, P123 (Aldrich)), following the similar method reported in the paper.¹² Aluminum butoxide (Aldrich) was used as an aluminum source. The Si/Al molar ratios of initial sol mixture were fixed as 5, 10 and 20. The copolymer template was removed from the as-synthesized sample by calcination at 600 °C in air (heating rate; 1 °C/min).

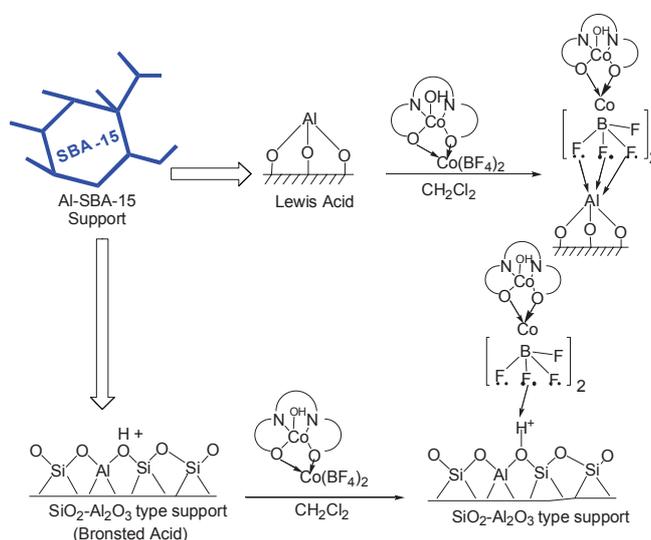
Similar to the synthesis of CMK-3, the reverse replica of Al-SBA-15 was fabricated by impregnation method using aque-



Scheme 1. Synthetic procedure for new homogeneous salen catalyst (A) and ionic type catalyst (B)

ous mixture of sucrose and sulfuric acid.⁴ Al-SBA-15 sample (1 g) was added to the solution obtained by dissolving 1.25 g of sucrose and 0.14 g of H_2SO_4 in 5 g of H_2O . The mixture was placed in a drying oven for 6 h at 100°C , and subsequently the oven temperature was increased to maintain at 160°C for 6 h. It turned dark brown during the treatment in the oven. The sample, containing partially polymerized and carbonized sucrose, was treated repeatedly at 100 and 160°C as above after the addition of 0.8 g of sucrose, 0.1 g of H_2SO_4 and 5 g of H_2O . The carbonization was completed by pyrolysis with heating up to typically 900°C under inert nitrogen. The carbon-silica/alumina composite obtained after pyrolysis was treated with a hot 25 wt % NaOH solution to remove the silica/alumina template. The template-free carbon product thus obtained was filtered, washed with ethanol, and dried at 120°C . The mesoporous carbon material will be denoted as C-SBA-15 in this work.

Chiral (Salen) cobalt complexes immobilized on mesoporous SBA-15. First, homogeneous chiral Co(III)-Co(BF_4)₂ salen (catalyst (A)) was prepared by mixing in 1:1 mole ratio of (*R,R*)-(-)-*N,N'*-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamino cobalt(II) and $\text{Co}(\text{BF}_4)_2$ salt under bubbling of air for 4 h in THF solvent. Evaporation of THF gave a solid in dark black color (yield; 98%). The BF_4 ion containing Co(III)- BF_4 salen (catalyst (B)) was synthesized by the oxidation of cobalt(II) salen ligand with ferrocenium tetrafluoroborate ($\text{Cp}^+(\text{BF}_4)^-$) in acetonitrile under air. The final catalyst (B) was obtained by washing the evaporated crude powder with *n*-hexane. The structures of parent cobalt (II) salen ligand, catalyst (A) and catalyst (B) are indicated in Scheme 1. The Al-containing mesoporous SBA-15 and its reverse replica C-SBA-15 were used as supports for immobilization of chiral catalyst (A) and (B). The procedure to anchor the chiral complexes on the surfaces of mesoporous supports is shown in Scheme 2. Heterogenized chiral salen catalysts were prepared by refluxing a solid acid Al-SBA-15 with the solution containing chiral catalyst (A) in MC for 4 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. The homo-



Scheme 2. Schematic representation of heterogenized chiral (salen) Co(III)-Co-(BF_4)₂ (catalyst(A)) on mesoporous Al-SBA-15 support

geneous catalyst (A) was also anchored on C-SBA-15 after loading of AlCl_3 on that carbon support. The procedure to impregnate AlCl_3 on C-SBA-15 was followed the method reported previously, except the calcination under air at 500°C .¹⁴

Characterization. The phase structure of Al-SBA-15 was determined by X-ray powder diffraction analysis (Phillips PW22XX and Rigaku DMAX 2500 diffractometer with $\text{Cu K}\alpha$ radiation). The microstructures of samples were characterized by field emission transmission electron microscopy (FE-TEM, S-4200). The nitrogen adsorption/desorption analysis was performed at -196°C by using a surface area and porosity analyzer equipment (Micromeritics, ASAP 2010). The coordination of Al on SBA-15 and C-SBA-15 (after impregnation of AlCl_3 and calcination) were characterized by solid ²⁷Al-MAS-NMR analysis (DSX 400 MHz Solid State Bruker NMR (at KBSI Daegu); 400 MHz with magic angle spinning at 10 kHz, $\pi/2$ pulse, 2 μs contact time, a repetition delay of 2s and 30000 scans). FT-IR spectra were recorded on a BRUKER IFS 48 spectrometer. The

anchored cobalt contents (salen amount) were determined by ICP-atomic emission spectroscopy (Optima 5300DV, Perkin-Elmer (40 MHz, 1.5 KV RF-generator)). UV spectra were recorded on UV-vis spectrophotometer (Optizen 2120 UV, Lab korea, Korea) interfaced with a PC using Optizen view 3.1 software for data analysis. The electron spectroscopy for chemical analysis (ESCA) data were obtained with a Sigma-Probe (Thermo VG, U.K.) spectrometer using Mg K α radiation as an excitation source ($h\nu = 1253.6$ eV). The binding energies for cobalt and oxygen were compared to those of reference cobalt(II) salen which was purchased from Aldrich.

General procedure for the catalytic reaction. The catalytic activities were evaluated for the asymmetric ring opening of terminal racemic epoxides such as (\pm) ECH by water as a nucleophile. In a representative reaction, the catalyst (1.5 mol % salen-loading/support), THF and (\pm)-ECH (0.93 g, 10 mmol) were charged in a flask (25 mL), and the reaction mixture was stirred in open atmosphere at ambient temperature. After addition of water (0.1 g, 5.5 mmol, 0.55 equiv), the resultant mixture was stirred for 20 h, and the conversion of epoxide and ee % (enantiomeric excess %) values of epoxide product were determined by GC using a capillary chiral column (CHIRALDEX, γ -cyclo-dextrin trifluoroacetyl, 30 m \times 0.25 mm i.d.).

Results and Discussion

Synthesis and characterization of Al-SBA-15 support. The mesoporous Al-SBA-15 having aluminum species was used as a support to immobilize the chiral salen complexes. X-ray diffraction analysis was carried out to investigate the structural feature of obtained Al-SBA-15, and the result is presented

in Fig. 1. X-ray powder diffraction at low angle for Al-SBA-15 sample gave the peak patterns corresponding to an irregular pore ordering, as evidenced by the disappearance of (110), (200) and (211) peaks. TEM images in Fig. 1 indicate that Al-SBA-15 has the disordered mesoscopic pore structure. For further characterization of the mesopore structure of Al-SBA-15, the nitrogen adsorption/desorption isotherm was determined. The N₂ isotherm of Al-SBA-15 showed the increase in uptake of nitrogen and the change in the shapes of hysteresis loops extending from P/P₀ = 0.4 - 1.0, indicating the presence of mesopores. In addition, the same characterization was performed for the sample of mesoporous carbon which was fabricated using Al-SBA-15 by replication process. The TEM image at high magnifications showed the disordered worm hole type mesopore channels. As can be seen in that TEM image, the mesopore structure of C-SBA-15 indicated almost the inverse replica of Al-SBA-15. The XRD pattern and the nitrogen adsorption/desorption isotherm of C-SBA-15 were same as compared to those of Al-SBA-15. These two materials were used as supports to immobilize the new homogeneous salen catalyst (A).

Characterization of homogeneous salen complexes. The structural feature of new catalyst (A) was characterized by the instrumental analysis before attaching it on the supports. It may happen to form the (B)-type catalyst unexpectedly, instead of catalyst (A), during the treatment of Co (II) salen by Co-(BF₄)₂·6H₂O. Therefore, the catalyst (B) was also synthesized separately by the reaction of ferrocenium tetrafluoroborate (Cp(BF₄)) with Co(II) salen ligand in order to distinguish the structural differences between the catalyst (A) and (B). UV, FT-IR and XPS analyses have been performed to determine the exact struc-

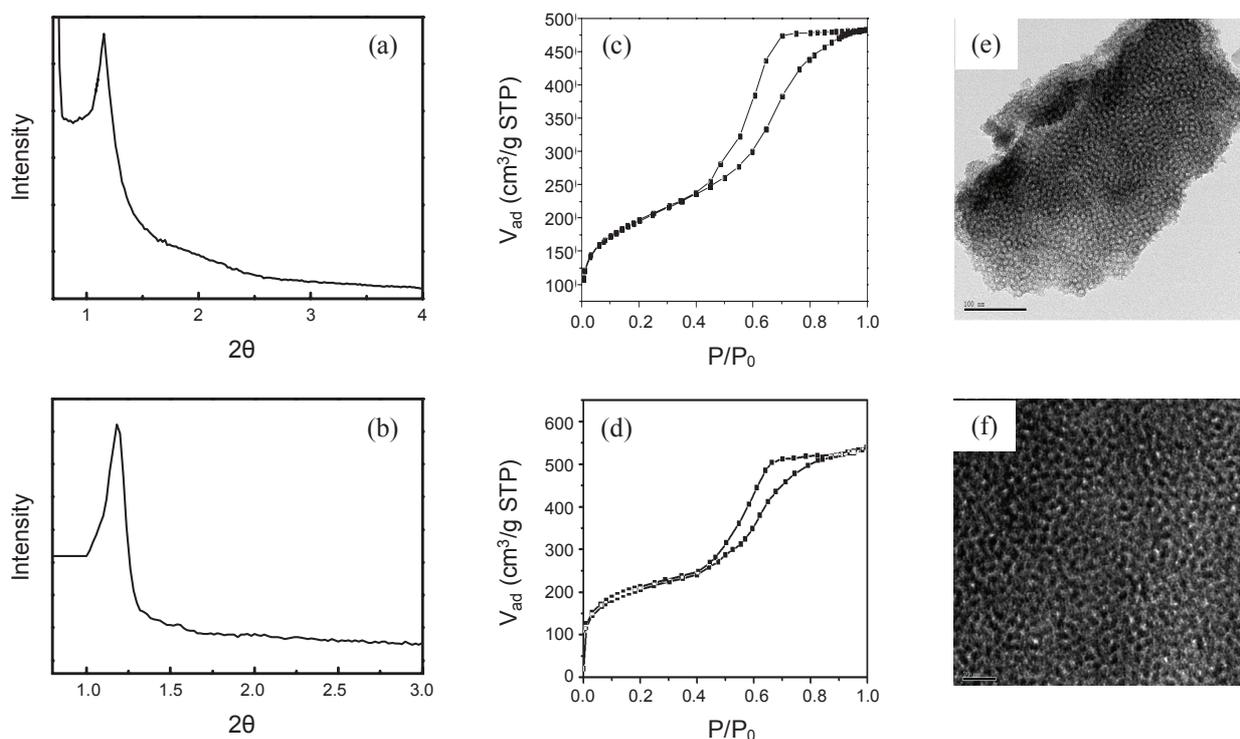


Figure 1. XRD pattern, N₂ isotherm and TEM image of mesoporous Al-SBA-15 (Si/Al = 10; (a), (c) and (e)) and C-SBA-15 ((b), (d) and (f)).

tures of both homogeneous catalysts.

The results of ESCA (XPS) can provide useful information about the element's oxidation state. Firstly, the full range spectrum of XPS for the homogeneous catalyst (A) was taken, and the result is shown in Fig. 2. Further elemental analysis data for catalyst (A) and (B) are summarized in Table 1 to show the differences between them. Those results indicated that not only the structure of catalyst (A) is completely different from the catalyst (B), but also $\text{Co}(\text{BF}_4)_2$ -salt was definitely combined to the cobalt-salen by the Lewis acidic action as reported previously.^{10,11} Because the inorganic salt of $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ was soluble in water, the presence of cobalt salt in the final product as a physical mixture can be ruled out after complete washing the catalyst (A) with water.

To identify the structure of new salen catalyst (A), the atomic states of each element such as cobalt and oxygen in the salen units were determined by XPS analysis, respectively. From the XPS spectra for cobalt species (Fig. 3), it was clear that the structural change of cobalt salen was created after the reaction between $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and cobalt(II) salen ligand. The position of each peak for binding energy on XPS spectra were slightly altered by the chemical state of emitting atoms. The starting Co(II) salen showed the XPS peak for cobalt at *ca.* 781 eV due to the presence of Co^{2+} ions. In the case of catalyst (A), the Co2p3 peak was found at *ca.* 780 eV, which is attributed to the Co^{3+} ion. It is clear that the binding energy of cobalt (Co2p3) was shifted from a higher to a lower value due to the change of cobalt oxidation state from +2 to +3 during the catalyst preparation under air. However, for the catalyst (B), +2 cobalt ion in the central position was also oxidized to +3 by balancing the increased +1 charge with tetrafluoroborate anion (-1), showing the peak at *ca.* 780 eV in the XPS spectrum.

Additionally the Co(II) salen ligand exhibited O_{1s} core level

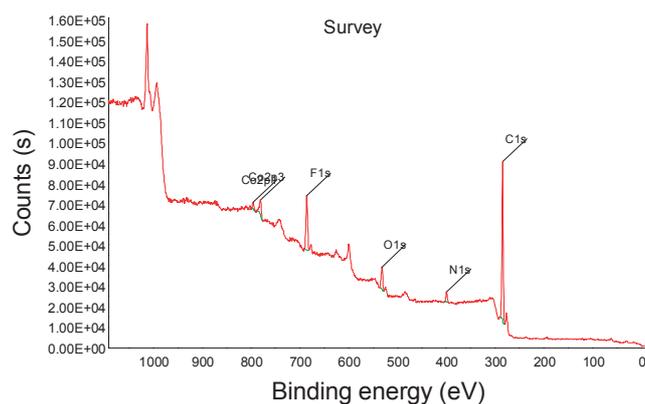


Figure 2. ESCA spectra for the homogeneous salen catalyst (A).

Table 1. XPS elemental analysis for catalyst (A) and (B)

Elemental	Catalyst (A)		Catalyst (B)	
	Theoretical	Determined	Theoretical	Determined
N/Co	1.0	1.1	2.0	2.1
C/Co	18	20	36	37
O/Co	1.5	1.4	2.0	2.0

peak at a binding energy of *ca.* 531 eV, while $\text{Co}(\text{BF}_4)_2$ salt containing cobalt-salen catalyst (A) showed a binding energy at lower value of *ca.* 530 eV as shown in Fig. 4. The observed change of 1 eV in binding energy (i.e. decrease from *ca.* 531 eV to 530 eV), for the Co(salen) containing $\text{Co}(\text{BF}_4)_2$ salt, could be attributed to the differences in the coordination environments of oxygen. In the case of catalyst (B), BF_4 anion is present to balance the positive charge of the cobalt-center like Jacobson catalyst [$\text{Co}^{\text{III}}\text{-OAc}$], which is +3; but there is no interaction between such an anion and O-atom in the salen-ligand. Therefore, the binding energies of O_{1s} should not vary between Co(II) salen and catalyst (B). Actually the catalyst (B) showed the same peak position for O_{1s} as the starting Co(II) salen ligand (with binding energy at 531 eV). These differences in core binding energies have been related to structural changes in the cobalt-salen-type complexes. Thus, the change in binding energy (O_{1s}) for salen catalyst (A) is attributed to the coordination of cobalt salt $\text{Co}(\text{BF}_4)_2$ to the O-atoms in the salen complex by the Lewis-acidic interaction as reported previously.

The characterization of the salen samples was carried out

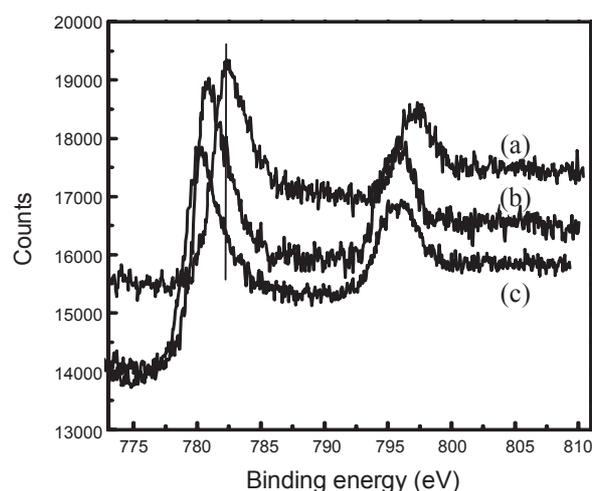


Figure 3. XPS data for cobalt: (a); Co(II) salen complex, (b); Co(III)- $\text{Co}(\text{BF}_4)_2$ salen (catalyst (A)), and (c); Co(III)- (BF_4) salen (catalyst (B)).

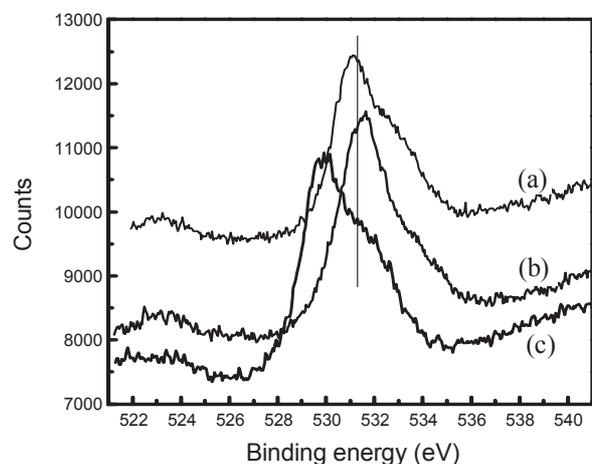


Figure 4. XPS data for oxygen: (a); Cobalt(II) salen complex, (b); catalyst (B), and (c); catalyst (A).

by UV-vis spectroscopy and the obtained UV spectra are shown in Fig. 5. The chiral Co(II) salen showed the characteristic absorption bands near 360 nm and 430 nm in the spectra. But for the salen catalyst (A), the characteristic absorption band of Co(II) salen at 430 nm was disappeared, and the new band near 390 nm was appeared on the UV-vis spectra due to the oxidation of Co(II) to Co(III) as same as the *Jacobsen* catalyst. The $\text{Co}(\text{BF}_4)_2$ salt showed the strong and broad one peak at 517 nm on UV-vis spectra, and this peak was not overlapped with the Co(II) salen and the catalyst (A). As a result, Fig. 5 is providing the evidence that the catalyst (A) is not a simple physical mixture of Co(II) salen ligand and $\text{Co}(\text{BF}_4)_2$ salt.

Immobilization of homogeneous salen complexes. The Co (salen) catalyst (A) having $\text{Co}(\text{BF}_4)_2$ group was easily attached onto the hydronium ions such as Bronsted acidic solids. For instance, $\text{SiO}_2\text{-Al}_2\text{O}_3$ support having Bronsted acid sites mainly could immobilize the catalyst (A) 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 (H^+) of support through the hydrogen-bonding. However, the

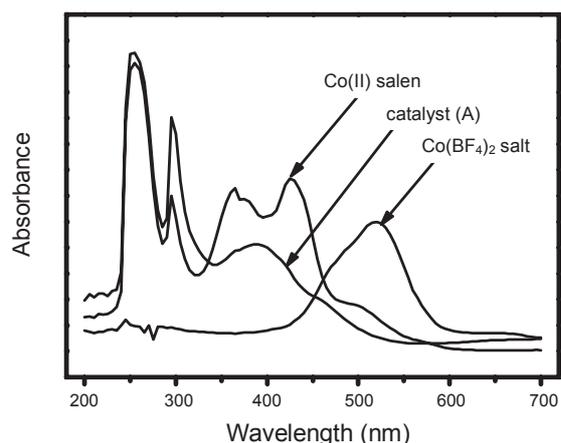


Figure 5. UV-vis analytical spectra for $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ salt, Cobalt (II) salen, and catalyst (A).

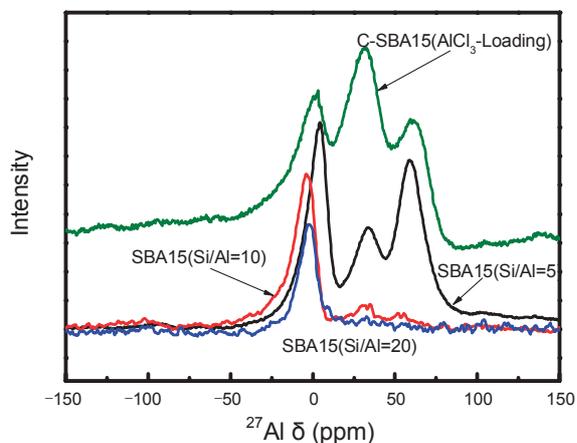


Figure 6. ^{27}Al MAS NMR spectra of SBA-15 (calcined at 500°C) containing the different contents of aluminum, and C-SBA-15 after loading of 20% AlCl_3 loading and calcination at 500°C in air.

adsorption of Co (salen) catalyst (A) on Lewis acid sites present on the support can not be ruled out as indicated in Scheme 2, since catalyst (A) was also attached strongly to the surfaces of Al-SBA-15 ($\text{Si}/\text{Al} = 10$) that has Lewis acidic sites only. In this work, ^{27}Al -MAS Solid NMR analysis was performed to distinguish the acid type of the solid supports. Fig. 6 shows the ^{27}Al -MAS-NMR spectra of Al-SBA-15 samples with the different aluminum contents. The strong peak at the chemical shift of 60 ppm is related to the aluminum atoms with tetrahedral coordination, and that peak at 0 ppm can be attributed to the octahedral coordinated aluminum (Lewis acidic sites).¹⁵ The peak at chemical shift of 20 ppm on the spectrum is interpreted as 5-coordinated Al site. For Al-SBA-15 ($\text{Si}/\text{Al} = 5$) sample with higher aluminum contents, three strong peaks were also found as similar as in the case of C-SBA-15. When Si/Al ratio of Al-SBA-15 was 10 and 20, no tetrahedral 4-coordination of Al was shown. However, the portion of 4- and 5-coordinated sites originated by Bronsted acids has become increased at the high loading amount of aluminum in Al-SBA-15. The result of Fig. 6 clearly shows that both Lewis and Bronsted type acid sites formed on the C-SBA-15 after loading of AlCl_3 . There are three distinct peaks on the spectra of 20 wt % AlCl_3 -loaded C-SBA-15 sample after calcination (Fig. 6).

The heterogenized chiral Co-salen catalyst (A) attached on the surfaces of mesoporous Al-SBA-15 were characterized by FT-IR analysis, and the obtained spectra are shown in Fig. 7. The characteristic peaks for homogeneous salen appeared at the position of 2958 - 2950, 2912, 1612 and 1535 cm^{-1} on IR spectra. However, the chiral (salen) cobalt (III) catalyst (A) anchored onto the mesoporous Al-SBA-15 (Fig. 7(b)) has exhibited the weak but similar absorption bands as the pure homogeneous chiral (salen) catalyst (A) on the IR spectra.

To identify the further structural characteristics of catalyst (A) before and after attachment onto the acidic sites, XPS spectra for F were taken, respectively, and the results are shown in Fig. 8. It is clear that the change of binding energy was observed due to the different environment in the fluorine species between the homogeneous and heterogeneous catalysts. For the homogeneous catalyst (A) containing $\text{Co}(\text{BF}_4)_2$ salt, the cha-

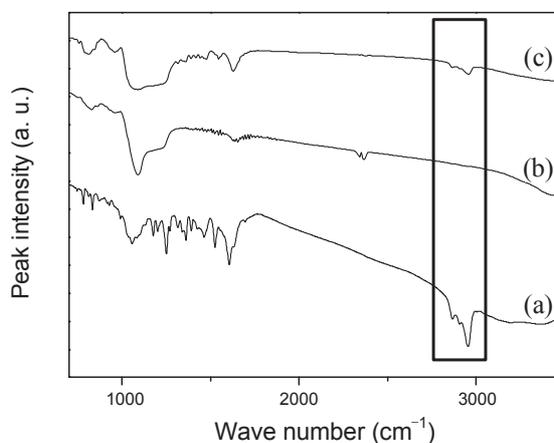


Figure 7. FT-IR spectra of (a) homogeneous catalyst (A), (b) pure Al-SBA-15 ($\text{Si}/\text{Al} = 5$), and (c) catalyst (A) immobilized on Al-SBA-15 ($\text{Si}/\text{Al} = 5$).

racteristic one peak was observed at the binding energy of 686 eV (Fig. 8(a)). However, in this case the eight fluorine species are present under the same environment. On the fluorine-XPS spectra for heterogenized catalyst (A), two peaks were resolved at 683.7 and 686.1 eV as shown in the spectra (b) and (c), indicating that the environment of fluorine has changed due to interaction between the acidic sites on the support. From this result, we could conclude that the homogenous catalyst was immobilized onto the acidic sites of Al-SBA-15 through electrostatic interaction with fluorine as indicated in Scheme 2.

Catalytic activity in asymmetric reaction. The trends in the activity and enantioselectivity of the heterogeneous salens were examined for the hydrolytic kinetic resolution (HKR) of epoxides, and the obtained results are summarized in Table 2. The chiral propylene oxide and ECH are very useful compounds as pharmaceutical intermediates including various anti-hypertensive drugs. Glycidol and styrene oxide also underwent enantioselectively in HKR by employing the immobilized catalyst (A).

The homogeneous catalyst (A) exhibited the superior catalytic activities relative to the homogeneous salen catalyst (B) as can be seen in Fig. 9. The catalyst (B) has the one cobalt site in the salen unit, but the catalyst (A) possess two cobalt cations in the same unit. The salen catalysts of dimeric structure or those bearing transition metal salts have displayed excellent reactivity for AKR of terminal epoxides in the previous works.

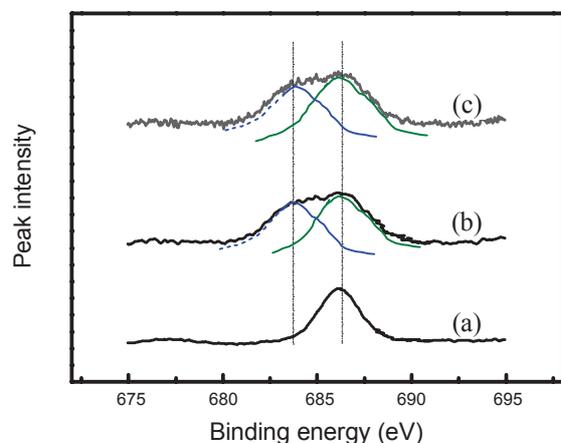


Figure 8. XPS spectra for fluorine: (a) homogeneous catalyst (A), (b) Catalyst (A) attached on Al-SBA-15, and (c) Catalyst (A) immobilized on aluminium coated C-SBA-15.

Table 2. HKR of terminal epoxides by homogeneous catalyst(A) and immobilized one on Al-ABA-15

Substrate	Catalyst	Time (h)	ee (%)
Propylene Oxide	Homogeneous Cata(A)	6	99.5
Epoxy Butane	Homogeneous Cata(A)	7	99.1
Propylene Oxide	Cata(A)/Al-SBA-15	10	98.7
Epoxy Butane	Cata(A)/Al-SBA-15	10	98.6
Glycidol	Cata(A)/Al-SBA-15	12	97.3
Styrene Oxide	Cata(A)/Al-SBA-15	23	92.6

*HKR: Epoxide; 1.0 mmol, water; 0.55 mmol, THF solvent for heterogeneous catalyst, room temperature Si/Al ratio of Al-ABA-15 was 5.

This result gives a strong support to a cooperative bimetallic mechanism involving a simultaneous activation of both epoxide and nucleophile by using our new catalyst (A). The differences in activities of catalyst (A) and (B) became severe when they were immobilized on the supports. It is remarkable that catalyst (A)/Al-BA-15 is much more active than catalyst (B)/Al-SBA-15 after attachment, exhibiting a high enantioselectivity relative to the homogeneous one. The catalyst (B)/Al-BA-15 was identified as less active in the HKR reaction. The superior catalytic activity of catalyst (A) anchored on the support was interpreted by the cooperative interaction of two cobalt ions in the same salen unit through the intra-molecular mechanism. Especially, since this catalyst is containing the fluorine species, simple and easy attachment on the acidic sites was established non-covalently.

In comparison, mesoporous C-SBA-15 support was used to anchor the same type of salen complexes. For this catalyst, a high catalytic activity was obtained. It is believed that the hydrophobic nature of carbon supports gave an improved activity in the hydrolytic kinetic resolution catalysis relative to the hydrophilic supports. The hydrophilic surfaces may provide the higher capability of water adsorption that was used as a reactant, leading the lack of water content needed for the reaction.

The effect of aluminum contents in Al-SBA-15 support on the reactivity was tested, and the results are summarized in Fig. 10. Higher reaction rates were observed, when the increasing concentration of active sites was allowed on the same amount of supports. The anchored amount of homogeneous catalyst (A) was proportional to the contents of Al present in the supports. That means a higher local population of salen complexes on the same surface area would be helpful to accelerate the reaction rates by the interaction between the catalyst units.

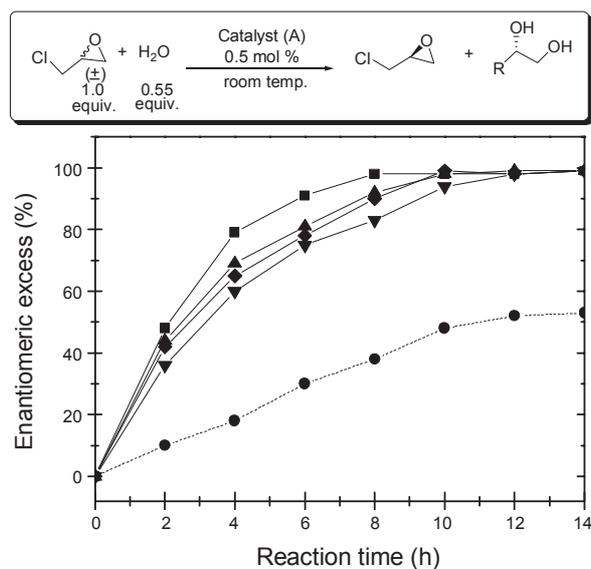


Figure 9. The catalytic activity of heterogeneous catalysts in the HKR of (±)ECH (■; homogeneous catalyst(A), ▲; catalyst (A) immobilized on C-SBA-15 (20 wt % Al loading), ◆; homogeneous catalyst (B), ▼; catalyst (A) immobilized on Al-SBA-15 (Si/Al = 5), ●; catalyst (B) immobilized on Al-SBA-15 (Si/Al = 5). 0.5 mol % salen to epoxide was added totally in the reaction mixture).

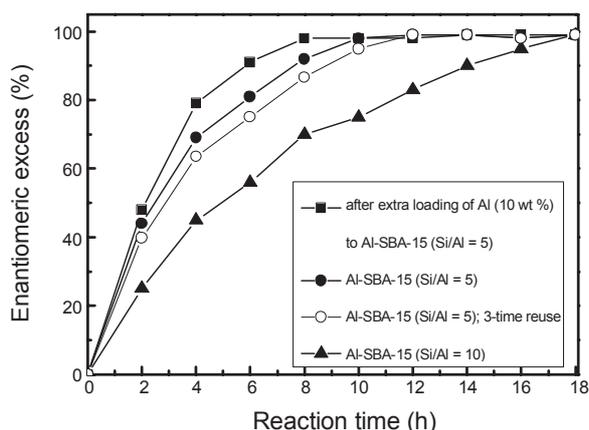


Figure 10. The effect of anchored contents of salen on Al-SBA-15 supports in HKR of (±)-ECH.

After three times reuse, the chiral salen catalyst (A) anchored on the mesoporous Al-SBA-15 has retained the high activity, but a slight decrease in enantioselectivity was found, indicating the some extraction of salen complex from the support as shown in Fig. 10. The catalyst was collected by simple washing with MC, THF solvents after reaction. The activity could be recovered after reattachment of homogeneous complexes on the reused catalysts.

Conclusions

The chiral salen cobalt (III) complexes combining $\text{Co}(\text{BF}_4)_2$ salt were newly synthesized and their structure was determined by the instrumental analyses. They were easily and non-covalently attached on the surfaces of mesoporous Al-SBA-15 silica through the electrostatic interaction between the fluorine in the salen and the acidic sites of support. Both Lewis and Bronsted acid sites generated by Al on the support were attributed to the

strong attachment of fluorine functionalized chiral salen complexes. The newly synthesized chiral catalysts showed high activity and enantioselectivity in the hydrolytic ring opening of terminal epoxides. Optically active terminal epoxides compounds with up to 99% ee were obtained in a high yield. Further studies to apply those heterogeneous catalysts in the asymmetric catalysis are currently underway.

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References

- Karlsson, A.; Stöcker, M.; Schmidt, R. *Micropor. Mesopor. Mater.* **1999**, *27*, 181.
- Demel, J.; Park, S.-E.; Cejka, J.; Stepnicka, P. *Catal. Today* **2008**, *132*, 63.
- Nur, H.; Hamid, H.; Endud, S.; Hamdan, H.; Ramli, Z. *Mater. Chem. Phys.* **2006**, *96*, 337.
- Kim, J. M.; Kwak, J. H.; Jun, S.; Ryoo, R. *J. Phys. Chem.* **1995**, *99*, 16742.
- Yang, H.; Li, J.; Yang, J.; Liu, Z.; Yang, Q.; Li, C. *Chem. Commun.* **2007**, 1086.
- Seebach, D.; Marti, R. E.; Hintermann, T. *Helv. Chim. Acta* **1996**, *79*, 1710.
- Vasylev, M. V.; Neumann, R. *J. Am. Chem. Soc.* **2004**, *126*, 126.
- Tokunaga, M.; Larrow, J. F.; Kakiuchi, F.; Jacobsen, E. N. *Science* **1997**, *277*, 936.
- Kawthekar, R. B.; Kim, G.-J. *Helvetica Chimica Acta* **2008**, *91*, 317.
- Kawthekar, R. B.; Bi, W. T.; Kim, G.-J. *Appl. Organometal. Chem.* **2008**, *22*, 583.
- Kawthekar, R. B.; Bi, W. T.; Kim, G.-J. *Bull. Korean Chem. Soc.* **2008**, *29*, 313.
- Kim, Y. S.; Lee, C.-Y.; Kim, G.-J. *Bull. Korean Chem. Soc.* **2009**, *30*, 1771.
- Lee, K.-W.; Lee, C.-Y.; Kim, G.-J. *Bull. Korean Chem. Soc.* **2009**, *30*, 389.
- Kim, Y. S.; Guo X. F.; Kim, G.-J. *Catalysis Today* **2010**, *150*, 91.
- Gan, J.; Wang, T.; Liu, Z.; Tan, W. *Stud. Surf. Sci. Catal.* **2007**, *170B*, 1567.