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Original article

카본/메조세공 실리카 복합 막을 응용한 키랄 에폭사이드의 가수분해반응과 동시 분리

최성대 · 전상권 · 박근우 · 양진영 · 김건중†

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Mesoporous Silica-Carbon Composite Membranes for Simultaneous Hydrolysis and Separation of Chiral Epoxide

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초 록

탄소와 다공성 실리카로 구성된 복합막을 용이한 방법으로 제작하고 이들 막을 활용하여, 키랄 에폭사이드와 키랄디올 화합물의 친수성/소수성 특성차이를 기초로 한 동시 합성 및 분리과정에 응용하였다. 막반응기에 도입한 키랄 Co(III)-BF_3형 살렌촉매는 ECH, 1,2-EB와 SO 등의 에폭사이드 가수분해반응에 대하여 높은 활성을 나타내었고 여러 차례의 재사용이 가능하였다. 광학순도가 높은 키랄 에폭사이드 생성물은 가수분해반응이 진행된 후에 촉매와 함께 유기용액상에서 취득되었다. 물에 용해되는 친수성의 1,2-디올은 키랄 살렌의 촉매작용에 의하여 가수분해됨으로써 생성되는데, 이들은 반응이 진행되는 동안 SBA-16 또는 NaY/SBA-16 실리카층을 통해 물층으로 확산되었다. 물은 막반응계에서 반응물이면서 동시에 용매로서 거동하였다. 연속흐름형의 막반응기를 적용함으로써, 고순도, 고수율의 광학이성체를 생성물로서 얻을 수 있었으며, 촉매는 큰 활성저하를 나타내지 않아 여러 차례 재사용이 가능하였다.

Abstract

The carbon/porous silica composite membrane was fabricated in a simple manner, which could be successfully for the simultaneous separation and production of chiral epoxides and 1,2-diols, based on their differences in hydrophilic/hydrophobic natures. The chiral Co(III)-BF_3 salen catalyst adopted in the membrane reactor system has given the very high enantioselectivity and recyclability in hydrolysis of terminal epoxides such as ECH, 1,2-EB, and SO. The optically pure epoxide and the chiral catalyst were collected in the organic phase after hydrolysis reaction. The hydrophilic water-soluble 1,2-diol product hydrolyzed by chiral salen diffused into the aqueous phase through the SBA-16 or NaY/SBA-16 silica composite layer during the reaction. The water acted simultaneously as a reactant and a solvent in the membrane system. One optical isomer was obtained with high purity and yield, and furthermore the catalysts could be recycled without observable loss in their activity in the continuous flow-type membrane reactor.

Keywords: *Chiral salen catalyst, membrane, SBA-16, optical isomer, separation*

1. Introduction

The syntheses of optically pure chemicals have gained significant potentials over recent years. Terminal epoxides are one of the important subclasses for the organic synthesis[1]. As a consequence, the preparation of optically pure terminal epoxides has long stood as a significant target for the synthesis of chiral building-block in the pharmaceutical industry[2]. Epichlorohydrine (ECH) is one of the attractive substrates, because the small chiral carbon molecules derived from ECH is extremely versatile as a synthetic intermediate. The catalytic ring opening reaction provides a practical manner for the preparation of stereochemically enriched terminal epoxides[3,4]. It was found that several systems based on the chiral cobalt-salen complexes were very efficient for the enantioselective synthesis of chiral epoxides by hydrolytic kinetic resolution (HKR). Typically HKR of racemic terminal epoxides with water catalyzed by chiral Co (III) salen complex may provide the highly enantioriched epoxides and 1,2-diols, as shown in Scheme 1[5-7]. The heterogeneous chiral catalysts offer practical advantages of the facile separation from reactants and products, as well as recovery and reuse. Much effort has been devoted not only to the development of active

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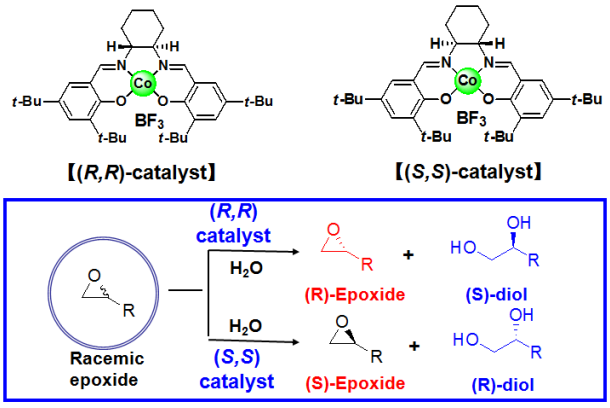

Scheme 1. The structure of catalysts and hydrolytic kinetic resolution system.

catalysts but also to finding the ways to enable the repeated use[8-11]. The reuse is especially important for chiral catalysts, which are usually more expensive than achiral ones. The chiral salen-based catalysts developed recently are appealing as good candidates for the development of recycling of chiral catalysts. Based on these facts, our attention was directed to the new fabrication of optically active catalyst systems desirable for repeated use without any treatment after reaction.

Recently, the development of membranes has drawn much attention in view of promising application as a separation tool as well as a catalytic reactor. Zeolite has been used as a useful component for formulating composite membranes, and zeolite membranes have been synthesized by in *situ* hydrothermal synthesis on the flat surfaces of supports. The unsupported self-standing films of zeolite have been obtained by traditional wet hydrothermal synthesis[12-15] or by solid-state transformation[16]. The catalytic membrane system represents one of the most promising areas for the application of membrane catalysis[17]. It allows to separate the reagents with markedly different polarities without the need for a mutual solvent and to increase the conversion of reactant. The catalytic reactors installed with inorganic membranes can increase the reaction conversion beyond the chemical equilibrium. We have synthesized zeolite crystals hydrothermally as a film form on the macroporous alumina support like Anodisc 47[18]. Those membranes could be used repeatedly for the simultaneous separation and HKR reaction of terminal epoxides after immobilization of chiral salen catalysts. However, in that system, it was difficult and limited to load the chiral catalyst at the suitable position. The high amount of catalyst must exist near the interface to contact with both biphasic reactants such as epoxides and water in the heterogenized catalytic system. Whereas, by introducing even the homogeneous chiral catalysts into the organic phase without anchoring, the contact between the catalyst and reactants went on smoothly at the interfaces of composite membrane.

In the batch type homogeneous hydrolytic reaction of epoxides, the diol compounds produced by the hydrolysis of epoxide should be evaporated at higher temperature for the separation from the homogeneous chiral catalysts. Consequently, this thermal treatment causes the decrease of chirality for epoxides and the deactivation of catalyst. However, if the isolation of diols from chiral salen catalyst can be performed successfully during the reaction in such a membrane reactor, the severe deactivation of catalysts can be ignored for further reuses. The chiral epoxides having a low boiling point can be isolated from the mixture of products at lower temperature without thermal shocks to salen catalysts by evaporation.

For those purposes, herein this study, the composite membrane was fabricated by attaching two layers of filters such as carbon and silica fiber filter impregnated by SBA-16 sol or NaY/SBA-16 sol. The simple coating of SBA-16 sol or NaY/SBA-16 sol on the silica filter paper is easier and more efficient method for the preparation of silica composite membrane as compared to the direct hydrothermal synthesis. Consequently HKR is simulated to happen at the interfaces where two reactants contact together in the presence of chiral catalyst by maximizing the hydrophobic/hydrophilic character of each layer in composite membranes. The biphasic organic/aqueous membrane reactor could provide the simultaneous separation of products as optically pure isomer. As the 1,2-diol product is collected in the aqueous phase by continuous diffusion during the hydrolysis reaction, the salen catalyst could be recovered and reused after isolation of chiral epoxide product by evaporation.

In this work, a continuous flow-type membrane reaction system was applied, and the Co (III) salen catalyst in membrane reactor has resulted in a very high yield and enantioselectivity for epoxides. To the best of our knowledge, the work reported here is the efficient simple route to synthesize the optically pure epoxides using a membrane reactor. Additionally, in this work, the spectral analysis of VCD to measure the enantiomeric excess % (%EE) values of chiral molecules was examined in the catalytic membrane system. Thus, we demonstrated that FT-VCD is an appropriate analytical tool to monitor the kinetics of reactions involving chiral molecules.

2. Experimental

2.1. Preparation of catalysts

In this work, the active chiral salen catalyst was prepared according to the procedure reported in the literature previously[8]. The compound of (1*R*,2*R*)-(-)-*N*,*N*'-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexane diaminocobalt (II) (Aldrich Chemical Co. Inc) was treated with a BF_3-$2H_2O$ in methylene chloride(MC) at room temperature under air for 2 h. The mixture was concentrated to dryness and washed with hexane. This catalyst will be denoted as Co(III)-BF_3, and that was adopted as a catalyst to investigate the effect of reaction conditions on the enantioselectivity in the asymmetric ring opening (ARO) reaction of terminal epoxides such as ECH, 1,2-epoxybutane (EB) and styrene oxide (SO) of racemic form by water in the membrane reactor. The ability of simultaneous reaction and separation in the membrane catalytic system was studied mainly in this work.

2.2. Membrane reactor system

Pure SBA-16 sol or the mixture of NaY powder and SBA-16 sol was coated on the silica filter paper (quartz microfiber filters QF1; Chmlab Co., diameter; 90mm, pore size; 1.6 μm, no binder) under the vacuum. The composite sample was dried at 100 ℃ for 24 h, and cal-

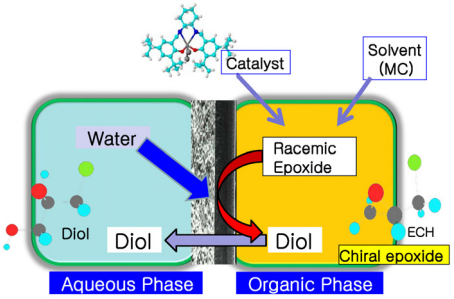

Figure 1. Silica/Carbon composite membrane system used in the simultaneous enantioselective hydrolysis and separation of epoxides.

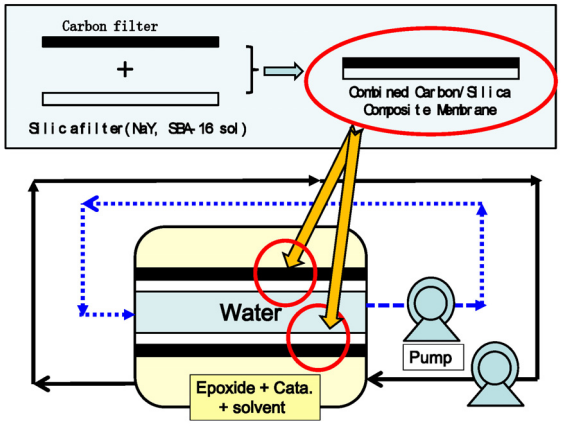

Figure 2. Schematic diagram for the continuous flow-type membrane system for the enantioselective HKR of epoxides.

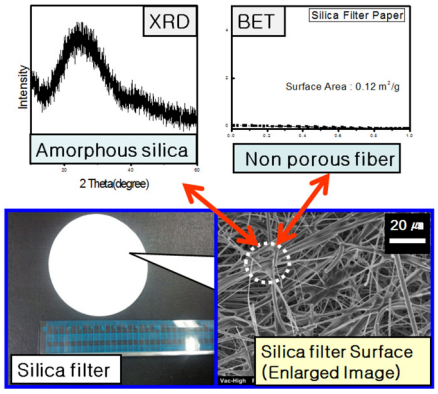

Figure 3. The analytical results for SEM, XRD and BET of pure silica filter paper used as a hydrophilic matrix.

cined in air at 600 ℃ with increasing heating rate of 5 ℃/min. The SBA-16 sol was filled in the gap between silica fibers by forming the thick films, and NaY zeolite powders were adhered on the surfaces of silica fiber matrix very strongly. This hydrophilic silica filter and the hydrophobic carbon filter were attached as one composite membrane layer. Ludox 40 (colloidal silica, Du Pont Co.) was used as a glue material to combine them. The aqueous phase and the organic phase were separated by membrane layer. The carbon/polyethylene (PE) fiber filter paper was used as a hydrophobic diaphragm in the fabrication of composite membrane matrix.

Figure 1 represents the configuration of membrane reactor system. One reaction vessel separated by the composite membrane was filled with water and the other with racemic epoxide in the presence of dichloromethane, as in Figure 1. The chiral salen Co (Ⅲ) catalyst was introduced into the organic phase in a biphasic membrane reactor wherein the two phases exist separately. The reaction was occurred at the interface of two composite membrane layers through the catalytic activation by chiral salen. However, because the chiral salen catalyst is insoluble in water, the chiral salen exists in the organic phase without penetrating into the aqueous layer during the reaction. As a result, this membrane reactor permitted the chemical reaction with the simultaneous extraction of products at the same time. The obtained epoxide product remained in the organic phase and the hydrophilic water-soluble 1,2-diols could diffuse into the aqueous phase across the silica composite layer.

The HKR of epoxides with water was performed at room temperature over the chiral Co (Ⅲ) salen catalyst in the membrane reactor. The continuous flow type reaction system applied in this study is represented in Figure 2. A counter-current flow was chosen for the circulation of two separated phases. The organic and the aqueous phases were separately circulated in the two circuits following the criteria that the organic phase (mixture of solvent, epoxide and chiral salen catalyst) was circulated along the side of carbon layer. The each solution was circulated by pumps, and the samples were taken for analysis at the corresponding reaction time. The %EE values in the products were determined by capillary GC using a chiral column (Chiral DEX-TM, Gamma-cyclodextrin trifluoroacetyl, 40 m × 0.25 mm i.d. (Alltec)). The crystallinity of treated sample was characterized by X-ray diffractometer (Rigaku DMAX 2500 diffractometer with CuKα radiation). Field emission transmission electron microscopy (FE-TEM, S-4200) and scanning electron microscopy (FE-SEM, JEM-2100F) were performed for the characterization of fabricated membranes. The porosity could be confirmed by BET (ASAP 2000/Protech) adsorption. The nitrogen adsorption and desorption analysis was performed at -196 ℃ by using a surface area and porosity analyzer equipment (Micromeritics, ASAP 2010). The samples were outgassed at 10^{-5} torr at 200 ℃ prior to measurement. The specific surface areas were calculated according to BET theory. The pore size was determined by BJH analysis. A dual-source, dual-polarization-modulated VCD spectrometer developed from a commercial FT-VCD spectrometer, the Chiral*IR* (ABB Bomem-BioTools, Quebec, PQ, Canada and BioTools, Inc., Wauconda, IL) was used to carry out IR and VCD measurements in the spectral range 800-2000 cm^{-1}. All spectra were collected at room temperature with a resolution of 4 cm^{-1}.

3. Results and Discussion

Figure 3 shows the SEM image of purely siliceous Quartz fiber filter paper used as a hydrophilic substrate. The filter paper was composed of silica fibers with a 3-dimensional network and the large void spaces between fibers. The silica fiber itself gave a very low BET surface area

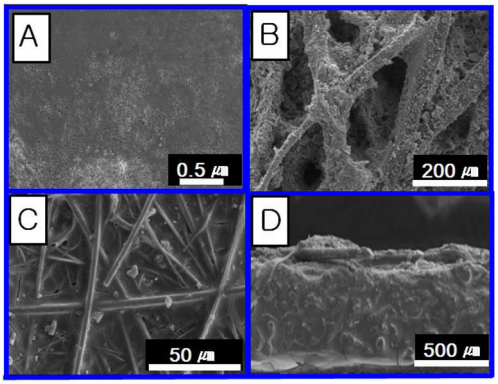

Figure 4. SEM images of silica fiber filter paper coated with SBA-16 sol (C, D) and the mixture of NaY particles and SBA-16 sol (A, B) under vacuum: A, C; surfaces, C, D; cross section (after calcination).

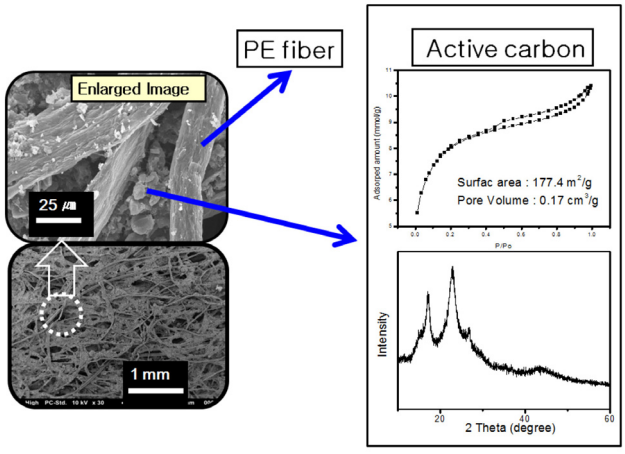

Figure 5. The analytical results for carbon filter paper.

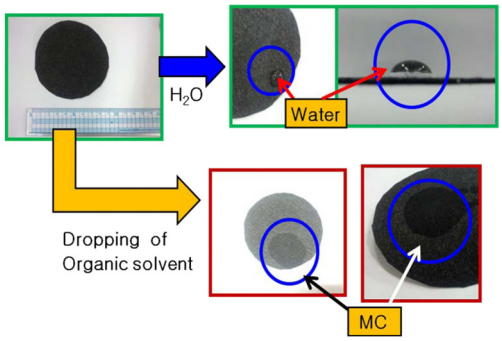

Figure 6. Wetting of water and methylene chloride on the surfaces of hydrophobic carbon filter paper.

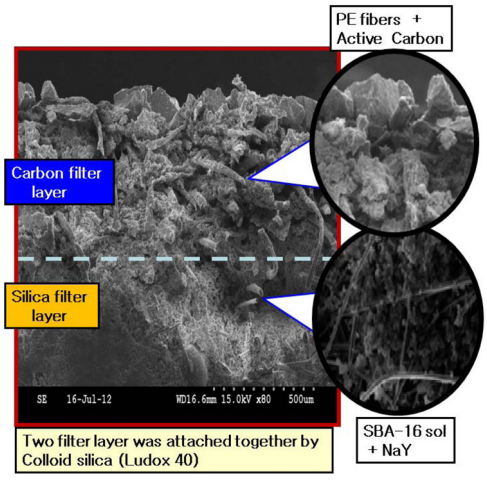

Figure 7. SEM images of two composite layers fabricated for membrane: Each carbon filter paper and silica filter paper was attached to combine as one composite membrane layer (Ludox 40 as a glue material).

less than 5 m^2/g, indicating that there is no pore channels in each fiber. In addition, Figure 3 shows the X-ray diffraction pattern of silica fibers. As shown in the result, for the diffraction pattern of silica filter paper, non crystalline phases were observed in the X-ray diffractogram. The pure SBA-16 sol was prepared, and it was coated on the surface of silica fiber support. After calcination of composite sample at 600 ℃ to remove the surfactant, SBA-16 solid was filled in the spaces between silica fibers by forming the thick films (Figure 4 (C), (D)). In addition, the mixture of NaY powder and SBA-16 sol was coated on the silica fiber support under the vacuum. The surfaces of fiber matrix were fully covered with NaY zeolite particles, and they were strongly adhered on the surfaces (Figure 4(B)). The gap between the fibers was not found any more on the filter paper surfaces (Figure 4 (A), (C)) as compared to those on the fresh silica fiber substrate (Figure 3). This hydrophilic silica filter was attached to the hydrophobic carbon filter paper to prepare one composite membrane layer. We have synthesized zeolite crystals hydrothermally in a film form on the macroporous alumina support like Anodisc 47[18]. However, the simple coating of SBA-16 sol or NaY/SBA-16 sol on the silica filter paper is easier and more efficient method for fabrication of silica composite membrane as compared to the direct hydrothermal synthesis. The silica composite membrane showed high BET surfaces due to the porosity of NaY and SBA-16 layer. In addition, the hydrophobic layer could be provided on the membrane by using the carbon filter paper. The purpose of incorporating this layer is for the complete separation between the aqueous and organic phases in the membrane system. The carbon filter paper is composed of PE fiber and active carbon powders. As can be seen in Figure 5, both the particles of active carbon and PE fibers are found in the SEM images. This substrate gave the porous characteristics due to the active carbon. The peaks for carbon were observed in the XRD pattern.

Figure 6 shows the wetting ability of water or organic solvent such as MC on the surfaces of carbon substrate. The hydrophilic water did not spread out, forming the droplet on the surfaces. However the organic solvents were adsorbed very fast into the carbon layer. This hydrophobic property of carbon layer avoided the diffusion of water into the organic phase, acting as a diaphragm in the membrane reactor system. Whereas, the silica filter papers coated by SBA-16 or NaY/SBA-16 sol were wetted very fast by water, because the surfaces of those silica composite are so hydrophilic. Each hydrophilic silica composite paper and hydrophobic carbon paper was attached and combined as one composite layer. Ludox 40 was used as a glue material to combine them. The typical cross-section of combined composite

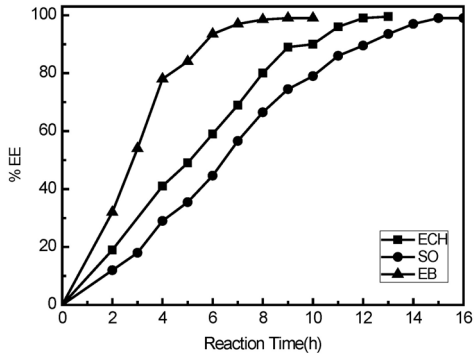

Figure 8. Enantioselectivities of Co (salen) catalyst for the HKR using different racemic epoxides in flow-type membrane reactor (0.5 mol% catalyst).

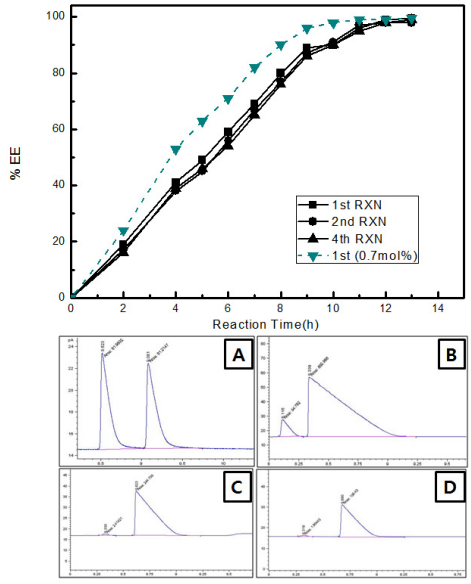

Figure 9. Asymmetric catalytic activity and recycle ability of Co (salen) catalyst in the continuous flow-type membrane system ((0.5 mol% catalyst for recycle reaction, ECH as a reactant). A~D; GC chromatograms ((A) 1st RXN 0 h (racemic ECH), (B) 1st RXN 8 h, (C) 1st RXN 12 h, (D) 4th RXN 12 h).

membrane can be seen in Figure 7. In the membrane system, the surface of NaY/silica fiber composite layer was set to contact with water, and the other side of carbon layer was wetted by the organic phase such as reactant epoxides and organic solvents. The aqueous phase and the organic phase were separated by that membrane.

The membrane system in which the chiral salen catalyst was immobilized near the interfaces of two solution phases has been applied for the synthesis and isolation of chiral epoxide[19]. In that system, it was very difficult and limited to load the chiral catalyst at the suitable position near the intermediate. The salen catalyst must exist near the interface to contact with both biphasic reactants such as epoxides and water. If the use of homogeneous chiral Co(III)-BF_3 catalyst itself without anchoring is applicable in the membrane reaction system, it may be an efficient and simple way.

In the homogeneous catalytic reaction, the obtained chiral epoxide

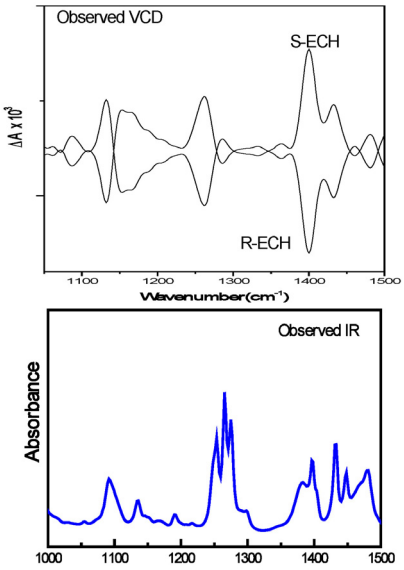

Figure 10. IR and VCD spectra of 1.0 M (R)-(-)-ECH and (S)-(+)-ECH in $CDCl_3$ solution.

can be isolated by evaporation since that compound has low boiling point less than diol compound formed by the hydrolysis of epoxide. The isolation of salen catalyst from highly viscous diol mixture became difficult in the recovery process. However, in our system, because the hydrolyzed product such as diol is removed by its diffusion into the water phase during the reaction, the reactant racemic epoxides can be supplied continuously into the organic phase chamber without regeneration of catalyst.

First of all, the trends in the reactivity and enantioselectivity of homogeneous (salen) Co (Ⅲ) catalyst were observed in the hydrolysis reaction of epoxides in the batch-type reactor. Various terminal epoxides such as ECH, EB and SO of racemic form were hydrolyzed enantioselectively over chiral Co(III)-BF_3 catalyst at 20 ℃. This type salen catalyst was selected as a suitable catalyst in our membrane reactor system.

The optically pure epoxides could be obtained continuously and enantioselectively in the carbon/silica composite membrane reactor using homogeneous chiral Co(III)-BF_3 salen catalyst. The results obtained for the ARO reaction, in the continuous membrane system, are summarized in Figure 8. The terminal epoxides such as ECH, SO and EB were readily catalyzed in high yield and high %EE. The %EE of epoxides in the organic phase has increased linearly with the prolonged reaction time. By applying the membrane system, the product separation became easier and the catalyst could be recycled without observable loss in activity. After reactions, Co (III) salen catalyst was not detected in the aqueous solution.

The catalyst in membrane could be recycled for many times by filling the reactant in the separated reactor chamber after evaporation of optically pure epoxides. The catalytic activity and selectivity of Co (salen) catalyst has not changed more or less after five times reuse in the hydrolytic reaction of ECH, as shown in Figure 9. Chiral Co(III)-BF_3 catalyst has exhibited the high optical purity of product (up to 99 %EE) during the repeated reuse in the hydrolysis reaction.

For the application VCD in determining the %EE of chiral epoxides, optically pure enantiomer (*R*)-(-)-ECH and (*S*)-(+)-ECH were analyzed

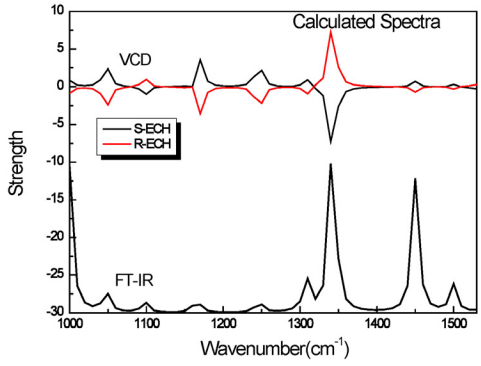

Figure 11. Calculated IR and VCD spectra of (*R*)-(-)-ECH and (*S*)-(+)-ECH.

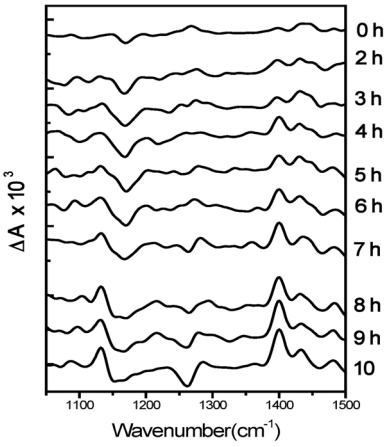

Figure 12. Changes in VCD sepectra of (S)-ECH with reaction time from 0 %EE (racemate) to 98 %EE.

by VCD as a standard sample. Figure 10 shows the IR and VCD spec tra of 1.0 M (*R*)-(-)-ECH and (*S*)-(+)-ECH determined in $CDCl_3$ solution. The peaks on IR and VCD spectra have slightly shifted in wavelength as compared to those obtained by calculation (Figure 11). However the characteristic peaks are found in the observed spectra, showing the up and down-direction like waves. The VCD peaks appear at the same position where the IR peaks does. (*R*)-(-)-ECH is showing fully reversed peaks in up-down direction at the same wave number as if a mirror image, as compared to (*S*)-(+)-ECH, indicating the opposite chirality in visual.

The VCD spectra of ECH product obtained during the hydrolysis reaction in the membrane system are shown in Figure 12. The change in %EE of (*S*)-ECH with prolonged reaction time was monitored by the changes in the VCD spectra. As the %EE of (*S*)-ECH has increased, the increase of peak intensity in VCD spectra was observed.

As similar as in the case of ECH, (*R*)-SO showed the opposite peaks in up-down direction as compared to (*S*)-SO at the same wave number, as can be seen in Figure 13. The determined VCD spectrum was almost same as that obtained by calculation. The analysis by VCD provides the practical way either for the determination of the optical purity and the absolute configuration of the sample. The determination of %EE by VCD provides some advantages with reasonable accuracy in the cases where more than one chiral species is present as a mixture.

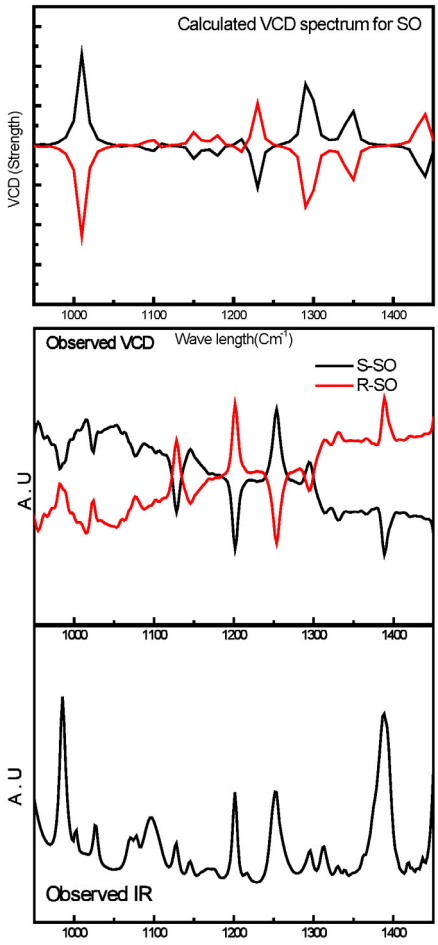

Figure 13. Observed and Calculated IR and VCD spectra of (*R*)-SO and (*S*)-SO.

4. Conclusion

The asymmetric hydrolysis of the terminal epoxides to chiral 1,2-diols using the membrane reactor system can be applied successfully by using chiral salen complex as a catalyst. The chiral Co(III)-BF_3 salen catalyst gave an high activity for HKR of terminal epoxides in the biphasic organic/aqueous condition. This enantioselective catalytic membrane system adopted in this study may be of interest for the application in the simultaneous reaction and separation of chiral products, based on their differences in hydrophilic/hydrophobic natures. The chiral catalysts in membrane could be recycled again by filling the reactants into the separated reactor. The catalytic activity and selectivity of Co (salen) complexes have not changed after more than 4 times reuse.

Acknowledgments

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