

폴리머 키랄 살렌을 함유한 메조세공 모더나이트의 비대칭 촉매 활성

곽소봉 · 김용석 · 라 올 · 김건중[†]

인하대학교 화학공학과
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Asymmetric Catalytic Activity of Mesoporous Mordenite containing Polymeric Chiral Salen Complexes in the Mesopore System

Xiao-Feng Guo, Yong-Suk Kim, Rahul B. Kawthekar, and Geon-Joong Kim[†]

Department of Chemical Engineering, Inha University, Incheon 402-751, Korea
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모더나이트결정 중의 실리카를 제어된 알칼리용액의 처리로 추출제거하여 중간세공이 형성되도록 하였다. 형성된 중간세공의 크기는 알칼리용액의 농도를 변화시킴으로써 조절할 수 있었다. 알칼리처리 후의 모더나이트 제올라이트 내부의 세공구조를 조사하였다. 새둥지형태의 중간세공을 형성시키기 위해서는, 알칼리용액 처리전에 모더나이트결정의 바깥표면을 티타니아로 코팅하는 것이 가장 효과적임을 관찰하였다. 모더나이트 내부의 중간세공에 고분자형의 코발트(III) 살렌착체를 “ship-in-a-bottle”법으로 가둔 촉매를 제조하였다. 이 고정화촉매를 물에 의한 에피클로로히드린의 산소고리열림반응에 사용하여, 촉매반응에서 높은 수율과 광학선택성을 얻을 수 있었다.

The formation of mesoporous pores in the microporous mordenite crystals was performed by controlled silica extraction on alkaline treatment. Inner tunable mesopore size could be controlled by changing the concentration of alkaline solution. The pore structure of mordenite zeolite was studied by instrumental analysis after alkaline-treatment. To obtain the cage type mesopores, Ti-coating on the outside mordenite crystals before alkaline treatment was investigated to be the most effective. Polymeric chiral salen Co (III) complexes were successfully encapsulated in mesoporous mordenite zeolite by “ship-in-a-bottle” method. The heterogeneous catalyst could be applied in asymmetric ring opening of epichlorohydrine by water. It showed very excellent enantioselectivity with a high yield in the catalysis.

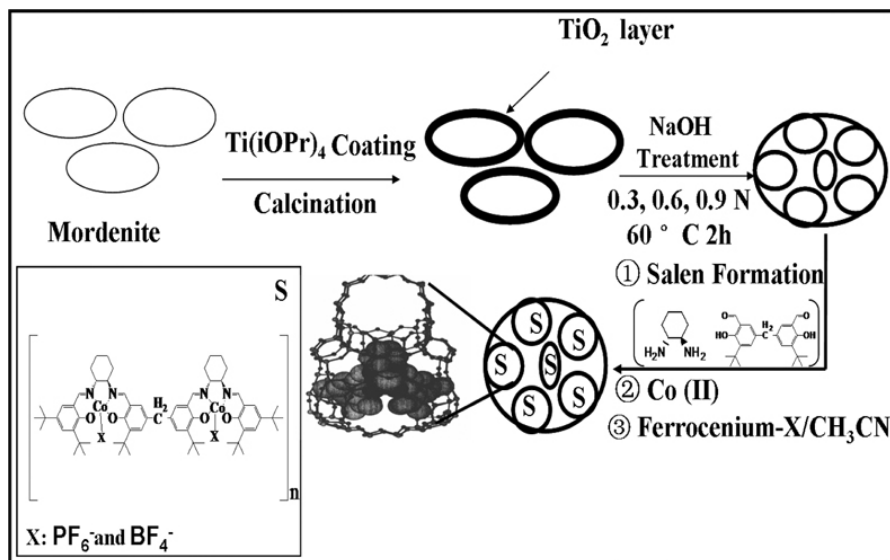
Keywords: mesoporous mordenite, chiral salen, ship-in-a-bottle, asymmetric catalysis

1. Introduction

Terminal epoxides are the most important subclass for the organic synthesis[1]. Consequently, the preparation of optically pure terminal epoxides has long stood as a most significant target for asymmetric chiral building-block synthesis[2]. Asymmetric ring opening reaction provides very efficient, scalable and practical manner to prepare stereochemically enriched terminal epoxides[3,4]. It has been found that several systems based on the polymeric chiral salen Co (III) complexes are very efficient for the highly enantioselective phenolic ring opening reaction of terminal epoxides (PKR)[5]. These active and selective salen- based homogeneous catalysts are appearing as candidates for heterogenization onto the polymer or inorganic supports. The heterogeneous catalysts can offer the practical advantages in the facile separation of products, as well as simple recovery and reuse of catalysts[6,7]. Various strategies have been explored to enhance the catalytic effi-

ciency of heterogenized salen complexes. Some approaches were demonstrated successfully to date in the asymmetric catalysis by using dimeric[8], dendrimeric[9], polymeric[10,11] and supported[12,13] type catalysts. The “ship in a bottle” synthesis has become an efficient method for immobilizing homogeneous catalysts within the solid matrix, particularly in microporous materials like zeolites. Over the last two decades, salen complexes have been successfully synthesized inside the supercages of X, Y, EMT zeolites[14,15]. However, the pore size and cage shape of microporous zeolites are strictly limited by their crystalline topology (usually < 1.5 nm) for other zeolites such as mordenite. It is impossible to encapsulate the polymeric chiral salen Co (III) complexes with relatively larger molecular size within the microporous zeolites by the “ship-in-a-bottle” method. Compared with microporous zeolites, mesoporous ones have larger pore size and cage, which provides possibilities for trapping larger molecules and more comfortable microenvironment for guest molecules[14]. The development of simple method in the synthesis of zeolites with a regular shape

[†] 교신저자 (e-mail: kimgj@inha.ac.kr)



Scheme 1. Schematic illustration for the synthesis of the polymeric chiral Cobalt (III) complexes encapsulated in mesoporous mordenite zeolites.

mesopore or cage like pore channel remains as a challenging objective. Preparation of mesoporous zeolite by dealumination and desilication method has been examined by acid or alkaline post-treatment[14,16].

In this work, a method to fabricate a novel mesoporous mordenite zeolite with tunable pore size and well defined cage shape was presented. A route to immobilized the polymeric chiral salen Co (III) complexes on mesoporous mordenite by the “ship-in-a-bottle” method will be demonstrated. Our main methodology for synthesis of mesoporous mordenite was desilication of Ti-coated outside mordenite zeolite (Ti-Mordenite) by the alkaline solution treatment. To the best of our knowledge, this method is most simple and efficient as compared to other procedures. A tunable pore size and well defined cage shape was attained by the methods. Polymeric chiral salen Co (III) complexes were successfully encapsulated in mesoporous mordenite zeolite by “ship-in-a-bottle” method. Heterogeneous catalyst was performed in asymmetric ring opening of terminal epoxides. Extremely high activity of heterogenized catalyst relative to homogeneous one was observed during the repeated use in the reaction.

2. Experimental

2.1. Synthesis of Mesoporous Mordenite Zeolite by Alkali Treatment

Titanium (IV) isopropoxide (0.72 g) was dissolved in isopropanol (30 mL) and the solution was stirred vigorously for 10 min at room temperature. H-type mordenite (2.0 g; Japan Referenc Catalyst, Si/Al = 8) was added to that solution. After 30 min stirring, methyl alcohol (10 mL) and deionized water (5 mL) were added, and it was stirred for additional 30 min. The solvents were evaporated under the reduced pressure and the residue was dried at 100°C in the oven for 12 h. The powder sample was calcined at 550°C for 5 h in air. This sample will be denoted as Ti-Mor. H-Mordenite or Ti-Mor was treated with NaOH solution in different concentrations (0.3 N, 0.6 N and 0.9 N) at 60°C for 1 h. The solid was recovered by filtration and washed with a hot deionized water. It was dried at 100°C in the oven for overnight.

2.2. Chiral Polymeric Salen Cobalt Complexes Encapsulated in Mesoporous Mordenite

Ti-Mor was used as a support for encapsulating the polymeric chiral salen Co (III) complexes. The procedure to encapsulate the chiral polymeric complexes in the mesoporous mordenite is shown in Scheme 1. First, (1R, 2R)-1,2-cyclohexanediamine (CHD) in tetrahydrofuran (THF) was introduced into the dry mesoporous mordenite zeolite. The dimeric dialdehyde was synthesized following the procedure reported by Jacobs *et al.*[17]. It was impregnated into the mordenite sample containing CHD in the pores, and the powder mixture was refluxed in ethanol solution. This treatment was sequentially repeated for 3 times to encapsulate the salen ligand as much as possible. The Co (II) ion was introduced into polymeric ligand/mesoporous mordenite by refluxing $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ in the mixed solution of methanol and toluene, and then powder was washed with solvents. The dried samples was treated with ferrocenium hexafluorophosphate or ferrocenium tetrafluoroborate in acetonitrile under air, respectively. The mixture was washed by acetonitrile and THF. These catalysts are denoted as Co (III)- $\text{PF}_6^-/\text{Meso-Mor}$ and Co (III)- $\text{BF}_4^-/\text{Meso-Mor}$.

2.3. Characterization

The phase structure of as-synthesized mesoporous mordenite was determined by X-ray powder diffraction analysis (Phillips PW22XX and Rigaku diffractometer with $\text{CuK}\alpha$ radiation). The morphology and microstructures of the as-prepared samples were characterized by field emission transmission electron microscopy (FE-TEM, S-4200), and field emission scanning electron microscopy (FE-SEM, JEM-2100F). The nitrogen adsorption and desorption analysis was performed at -196°C by using a surface area and porosity analyzer equipment (Micromeritics, ASAP 2010). The samples were outgassed at 10^{-5} torr at 200°C prior to measurement. The specific surface areas were calculated according to BET theory. The pore size was determined by BJH analysis. FT-IR spectra were recorded on a BRUKER IFS 48 spectrometer.

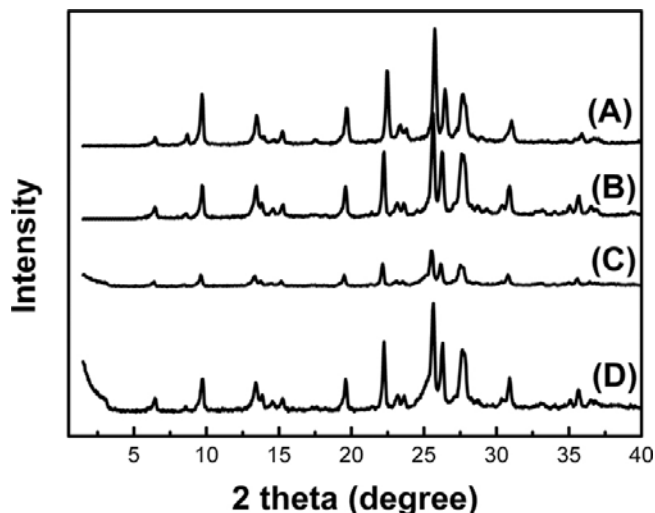


Figure 1. X-ray diffraction pattern of the parent H-mordenite (A), Ti-Mor (B), 0.9 N NaOH treated H-mor (C), and 0.9 N NaOH treated Ti-Mor (D).

2.4. General Procedure for Catalytic Experimental

In a representative reaction of epichlorohydrin (ECH) and water, the catalyst (0.4 mol% salen-loading/support), THF and (±)-ECH (0.93 g, 10 mmol) were charged in a 25 mL flask and the reaction mixture was stirred in open atmosphere at ambient temperature. After addition of water (0.99 g, 5.5 mmol), the resultant mixture was stirred for 24 h. During the reaction, the ee% of product ECH was monitored by Gas Chromatography using a chiral column (CHIRALDEX G-TA, 40 m 0.25 mm).

3. Results and Discussion

X-ray diffraction analysis was carried out to investigate the structural changes in mordenite zeolite upon alkaline treatment. Alkaline-treated mordenite without Ti-coating (H-Mor) exhibits big changes in the diffraction patterns as compared to the parent mordenite as shown in Figure 1. Some peaks disappeared or the intensity of peaks became decreased for H-Mor, which implies some destructions in the crystal lattice. The intensities of peaks are decreased generally with increasing the alkaline concentration in treatment. Whereas, alkaline-treated Ti-coated mordenite (Ti-Mor) showed very similar X-ray pattern to that of untreated zeolite (Figure 1). The Ti-Mor has resulted in no severe collapse of crystal structure during the dissolution of silica inside the crystal by alkaline solution. Because titania is insoluble to alkaline solution, that layer coated on the surfaces of mordenite crystal can protect the fast dissolution from the outside and may improve the tuning opportunities of selective mesopore formation. The alkaline-treated mordenite samples exhibited the broad peak at small angles less than 2 degree, indicating the formation of mesopores in the crystals.

The SEM images for representatives of NaOH-treated mordenite and the parent zeolites are shown in Figure 2. The morphological changes of zeolite during the HF treatment appeared quite crucial. Even after treatment of H-Mordenite with 0.9 N-NaOH, their crystal morphology

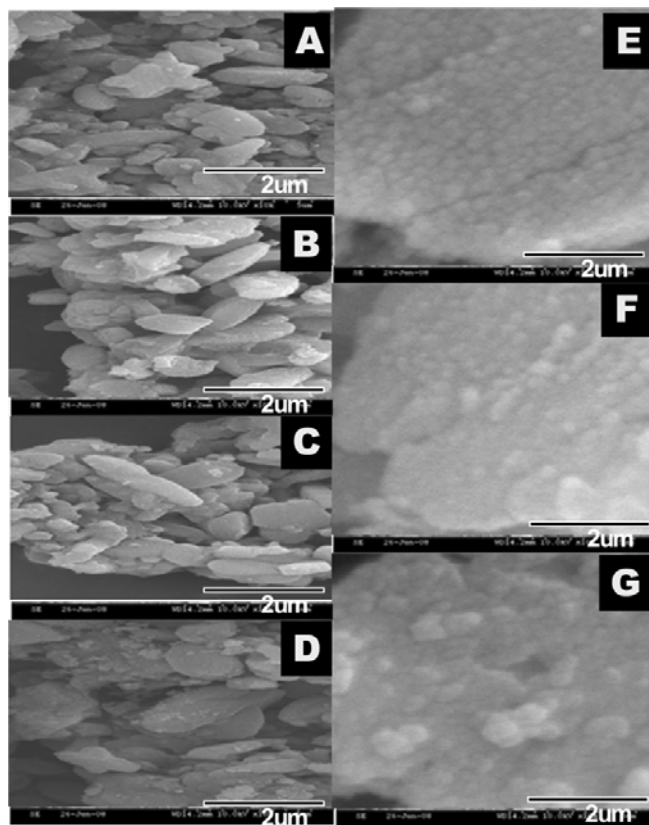


Figure 2. FE-SEM images of the parent H-Mordenite (A), 0.3 N NaOH treated Ti-Mordenite (B), 0.6 N NaOH treated Ti-Mordenite (C), 0.9 N NaOH treated Ti-Mordenite (D), 0.3 N NaOH treated Mordenite (E), 0.6 N NaOH treated Mordenite (F), 0.9 N NaOH treated Mordenite (G).

was still maintained, but a deep corrosion of surfaces was observed. However, the morphology of Ti-coated mordenite was almost similar before and after alkaline treatment.

To investigate the pore structure of mordenite after alkali-treatment, nitrogen adsorption/desorption experiment was performed (Figure 3). The parent mordenite showed the type I isotherm (Figure 3A), indicating they have only the micropores. Micro/Meso-scopic bimodal pore system was observed in the samples treated by NaOH solution. For the Ti-Mor sample treated by 0.6 N and 0.9 NaOH solution, the shape of hysteresis loops turned to be of type IV, which were generally obtained with adsorbents having slit-shaped or cage-like pores. Pore structural parameters of NaOH-treated Mordenite and the parent ones are shown in Table 1. The adsorption capacity (pore volume) was increased with the increasing alkaline concentration which was adopted to make a mesopores inside the mordenite. The large surface area, pore volume and a very big mesopore size were formed in the desilication process of Ti-Mor by the treatment of 0.6 N or 0.9 N-NaOH solution. The range of pore size distribution inside the Ti-Mor has changed from about 9 to 11 nm.

The images of mordenite samples analyzed by FE-TEM are shown in Figure 4. The parent mordenite showed no mesopores within the microporous crystal (Figure 4A). Many mesopores inside the Ti-Mor crys-

Table 1. Pore Structural Parameters and Si/Al, Si/Ti Molar Ratio, Recovery Yield of Alkaline-treated and Parent Mordenite

Zeolite sample	NaOH concent. (Normal)	Specific surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore size (Å)	Recovery yield (%)	Si/Al (molar ratio)	Si/Ti (molar ratio)
H-mordenite	-	850.0	0.340	6.0	100	7.7	0.0
H-mordenite	0.3	626.8	0.320	32.5	88	6.9	0.0
H-mordenite	0.6	589.5	0.34	39.6	72	5.8	0.0
H-mordenite	0.9	526.9	0.364	45.6	62	5.1	0.0
Ti-mordenite	-	824.6	0.325	5.8	100	7.7	10.2
Ti-mordenite	0.3	660.1	0.640	69.3	92	7.4	7.4
Ti-mordenite	0.6	614.2	0.649	94.9	89	7.1	7.0
Ti-mordenite	0.9	436.0	0.652	109.4	85	6.8	6.6

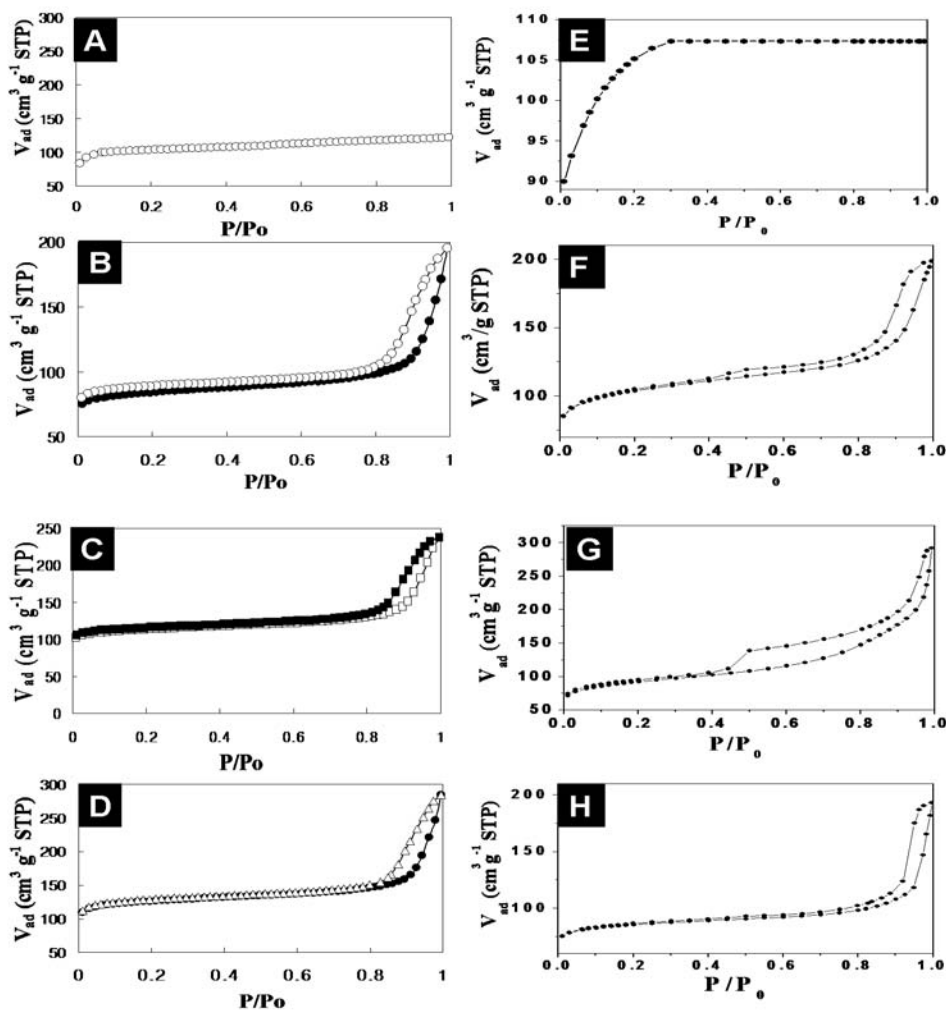


Figure 3. Nitrogen adsorption/desorption isotherm of the parent H-Mordenite (A); 0.3 N NaOH treated Mordenite (B); 0.6 N NaOH treated Mordenite (C); 0.9 N NaOH treated Mordenite (D); Ti-Mordenite (E); 0.3 N NaOH treated Ti-Mordenite (F); 0.6 N NaOH treated Ti-Mordenite (G); and 0.9 N NaOH treated Ti-Mordenite (H).

tals were formed by the treatment of NaOH solution from 0.3 N to 0.9 N, showing clearly that the volume of mesoporous channels was increased with the increasing the concentration of NaOH solution under the same treatment conditions. Ti-coating on the outer surfaces of zeolite was found to be the most effective and necessary for the formation of cage-like big mesopores within the mordenite crystal through the al-

kaline solution treatment. The coating layer of Ti on mordenite may protect the desolution of outer surfaces, and the partial leaching in the crystal lattice happened mainly at the inside of mordenite.

The homogeneous polymeric chiral (salen) cobalt complexes and the heterogeneous ones encapsulated in the mesoporous mordenite were characterized by FT-IR analysis (Figure 5). It is clear that the bulk pol-

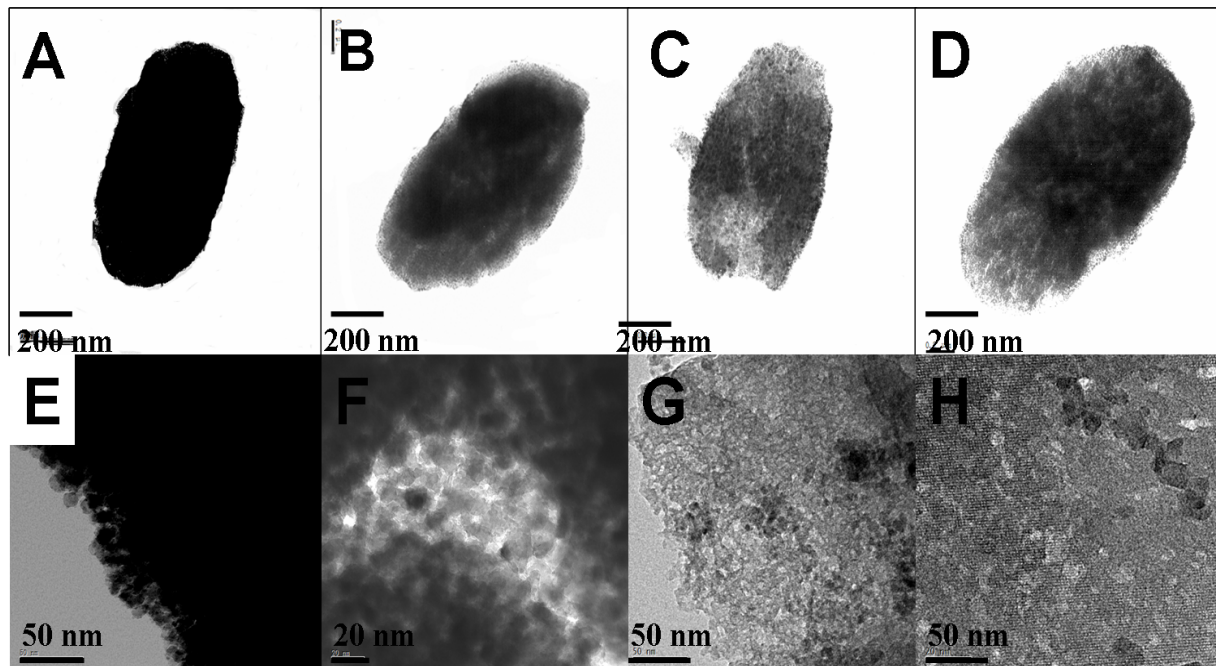


Figure 4. FE-TEM images of the parent H-Mordenite (A); 0.3 N NaOH treated Ti-Mordenite (B), (E); 0.6 N NaOH treated Ti-Mordenite (C), (F); 0.9 N NaOH treated Ti-Mordenite (D), (G); and 0.6 N NaOH treated H-Mordenite (H).

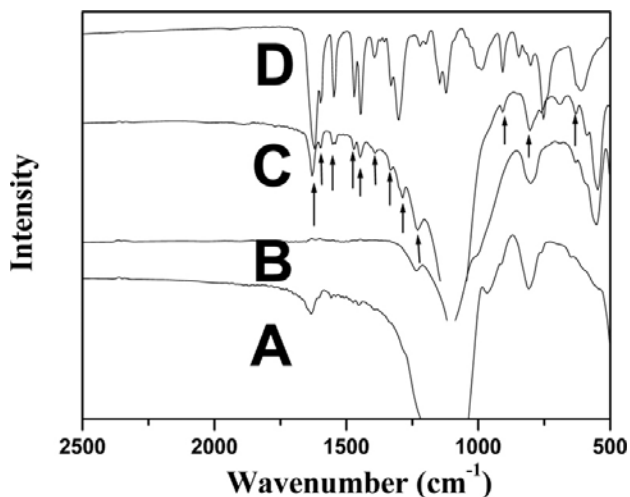


Figure 5. FT-IR spectra of polymeric chiral Cobalt (III) complexes encapsulated in parent mordenite (A), parent H-Mordenite itself (B), the chiral Cobalt (III) complex encapsulated in mesoporous Mordenite (C), and homogeneous chiral Cobalt (III) complex (D).

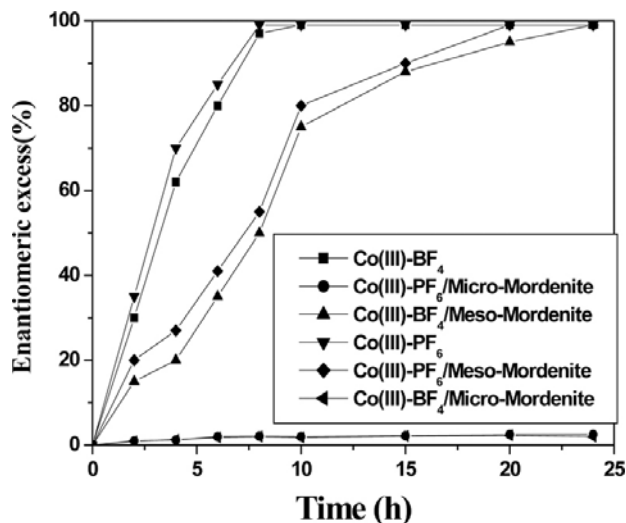
ymeric chiral (salen) cobalt (III) complexes (@15 Å) can not be introduced into the microporous channel of parent mordenite (@6 Å). The characteristic peaks for homogeneous polymeric chiral salen complex (III) appeared at the position of 2958-2950, 2912, 1612 and 1535 cm^{-1} . However, the chiral (salen) cobalt (III) complexes entrapped in the Ti-Mor (Figure 5(C)) exhibited the similar absorption IR bands as the pure homogeneous polymeric chiral (salen) complex (Figure 5(D)), showing that the chiral (salen) cobalt (III) was successfully encapsulated in the mesopore channels of Ti-Mor.

The activities of heterogenized catalysts were examined in the asym-

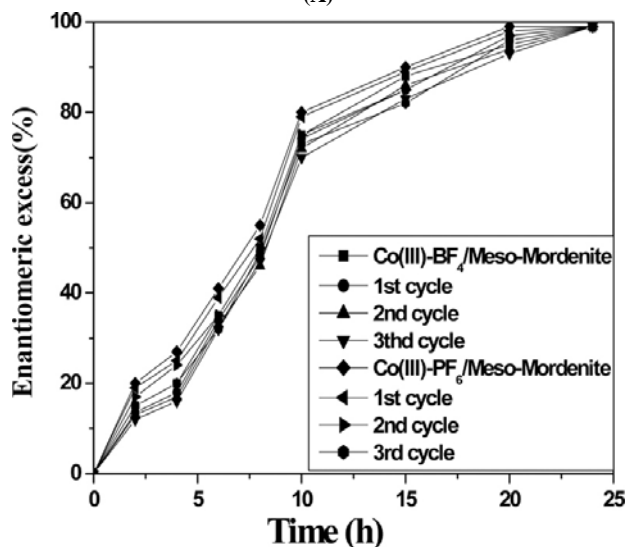
metric ring opening reaction of ECH by water, and the result is shown in Figure 6(A). It is clear that the salen catalyst oxidized by ferrocenium hexafluorophosphate exhibits the higher activity than with ferrocenium tetrafluoroborate. Optically active ECH (> 98% ee) was obtained in a high yield. Recyclability of chiral Co (III) salen complexes encapsulated in mesoporous mordenite zeolite was examined in the asymmetric ring opening reaction of racemic ECH epoxide. As shown in Figure 6(B), the Co (III)-PF₆/Meso-Mor showed higher recyclability than catalyst treated with and Co (III)-BF₄/Meso-Mor. After three times of reuse, the heterogenized salen catalysts have retained the high catalytic activity and enantioselectivity without further regeneration (up to 99% ee), but needed longer reaction time.

4. Conclusion

Mordenite type zeolite was treated with NaOH solution to introduce mesoporous channels in the microporous crystals. Inner mesopore size could be controlled from 3 to 11 nm by changing the concentration of alkaline solution. To obtain the cage type mesopores, Ti-coating on the outside mordenite crystals before alkaline treatment was investigated to be the most effective. By titanium oxide coating, the yield to the obtained mesoporous mordenite has increased more than 80%, and the big pore size was formed in side the crystals. The chiral polymeric salen cobalt (III) complexes encapsulated in the mesoporous mordenite by 'ship-in-a-bottle' method showed a high activity in the asymmetric catalysis (up to 99% ee). These heterogenized salen catalysts also retained the high catalytic activity and enantioselectivity after repeated use without regeneration.



(A)



(B)

Figure 6. The catalytic activities (A) and catalytic recyclabilities (B) of Co (III)-(PF₆) polymeric salen complex and Co (III)-(BF₄) polymeric salen complex encapsulated in the mesoporous mordenite.

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