SYNTHESES AND APPLICATIONS OF ZEOLITES
WITH BIMODAL MICRO/MESOSCOPIC AND
MESO/MACROSCOPIC STRUCTURES.

2006年 2月

仁荷大學校 大學院
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主審____________________

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委員____________________
ABSTRACT

Microporous materials with pore diameters less than 1.5nm have thermal, hydrothermal stability and chemical resistance. Although their material characteristics are very excellent as a catalysts, they have a limitation to process large molecules in a nanometer level. On the other hand, the pore size of MCM-41 and SBA-15 is bigger than that of Zeolite. However, Mesoporous structure of zeolite readily destroyed especially when exposed to steam at high temperature or to boiling water.

First, A route of synthesize ZSM-5 and TS-1 crystals with a bimodal micro/mesoscopic pore system has been developed in first study; the successful incorporation of the mesopores within the ZSM-5 structure was performed using tetrapropylammonium hydroxide(TPAOH)-impregnated mesoporous materials containing polystyrene-divinylbenzene nanotubes in the pores, which were encapsulated in the ZSM-5 crystals during a solid rearrangement process within the framework. Such mesoporous ZSM-5 zeolites can be readily obtained as powders, thin films, or monoliths.

Second, A route of synthesize porous materials with a bimodal macro/mesoscopic pore system has been investigated in second work;
Polystyrene with sub-micrometer size was used as a template in the synthesis. The resulting mesoporous silica wall replicated inversely the morphology of polystyrene template and had highly ordered three-dimensional arrays of macro pores. Large and moldable meso/macro porous silica monoliths could be obtained in centimeter scale by using monodispersed polystyrene beads and PEO-PPO-PEO/SBA-15 sol solutions. These bimodal structured porous silicates have been used as supports for asymmetric kinetic resolution of racemic epoxides to synthesize optically pure epoxide.
요약

세공크기가 1.5nm이하인 microporous 물질은 열적으로나 수분 및 화학적인 영향에 대하여 상당히 안정성을 갖고 있다. 그러나 이러한 microporous 물질의 특성은 촉매로써는 우수하다세공의 크기가 작다는 단점이 있다. 반면에 큰 세공을 갖고 있는 MCM-41이나 SBA-15의 경우는 이러한 제올라이트에 비하여 세공은 크지만 끓는 물이나 혹은 증기에 의해서 mesoporous 세공구조가 무너지는 단점이 있다.

첫번째로 이러한 micro/mesoporous 골격을 동시에 가지고 있는 ZSM-5 및 TS-1의 결정을 합성하는 방법을 소개하고자 한다.

ZSM-5와 mesopore의 성공적인 복합물의 합성은 세공 내에 polystyrene-divinylbenzene 나노튜브를 성장시키고 여기에 ZSM-5의 전구체 역할을 하는 TPAOH를 적셔서 반응하는 연속적인 반응을 통한 반응으로 mesoporous물질이 제조합과정에서 ZSM-5에 의해 감싸질 수 있게끔 유도한 방법을 이용했다. 이러한 micro 및 meso구조를 가지고 있는 물질은 powder나 얇은 film 또는 monolith 형태 등으로 얻을 수 있다.

두번째로 meso/macroporous 구조를 가지는 다공성물질을 합성하는 방법을 소개하고자 한다. 이러한 합성에서는 마이크로
미터 이하의 사이즈를 가지는 Polystyrene을 주형으로 사용하였 다. Polystyrene 주형 조직의 빈 공간에 mesoporous 물질을 채워 넣은 결과로 3차원 구조의 잘 정렬된 macropore 구조가 형성되었다. 단분산 Polystyrene 구체와 PEO-PPO-PEO/SBA-15 졸 용액을 이용하여 센터미터 사이즈의 크기로 주조가 가능한 meso/macroporous 실리카 단일체를 얻을 수 있었다. 이러한 두 가지 시스템의 세공구조를 가지는 규산염을 라세믹 에폭사이드로부터 광학적으로 순수한 에폭사이드을 얻어내는 비대칭 반응의 담채로서 사용하였다.
Chapter 1

Syntheses of ZSM-5 and TS-1 zeolites with bimodal micro/ mesoscopic structures.

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Chapter 1.

Syntheses of ZSM-5 and TS-1 zeolites with bimodal micro/ mesoscopic structures

1. Introduction

Microporous materials with pore diameters less than 1.5 nm have received much interest due in large part to their material characteristics such as large internal surface area, unique pore structure and adsorption capacity and controllability [1-5]. However, they have one limitation as catalysts, regarding their pore sizes that are not efficient to process large molecules in a nanometer level. Consequently, recent research efforts have been paid to the synthesis of nanoporous or mesoporous materials with large pore sizes and uniform pore distribution [6-12]. Obviously, significant advances of the physicochemical properties of these materials can be expected when the crystalline zeolites are incorporated into the mesoporous frameworks. Much recent research effort has been paid to the
synthesis of the micro- and mesoporous composites by various procedures [13-19]. The specimens prepared by those researchers exhibited the micro- and mesoporosity with the improved hydrothermal stability.

Recently, Jacobson et al. have synthesized mesoporous ZSM-5 crystals by restricting the crystallization of the zeolites to the mesopores resulting from the packing of the nanosized carbon particles [20]. It was possible for the zeolites to grow around the carbon particles of the inert matrix within the whole pore system. The mesopores can be created by combustion of carbon particles. Although this leads to mesoporous single zeolite crystals, the resulting pore size distribution was broad. Furthermore, only few useful carbon black materials are available and careful control of the crystallization conditions is necessary to avoid formation of nonmesoporous zeolite crystals.

Many types of mesoporous carbons have been produced using inorganic templates such as zeolites, silica sols, SBA-15, MCM-48 and solid core/mesoporous shell (SCMS) silica spheres. The structure of nanoporous carbons is an inverse replica of the silica templates after dissolution of them using HF or NaOH solution.
We have synthesized the mesoporous ZSM-5 zeolites by the crystallization of silica framework of TPAOH-impregnated mesoporous precursors (MCM-41 and SBA-15), containing nanostructured carbons in the pore channels [21]. Subsequently, small zeolite crystals grow into the large single crystals, encapsulating the carbon fibers present in the pores of mesoporous templates. In that case, the alumina sources must be implanted onto the silica templates for the polymerization of phenol and formaldehyde (or furfuryl alcohol). As a result, this method is not helpful for the synthesis of alumina free zeolites such as TS-1. Herein we report the simple method to synthesize silicalite and TS-1 zeolite with micro/mesoscopic pore structures using SBA-15 and Ti-SBA-15 as templates. In the synthesis, the porous walls of siliceous SBA-15 and Ti-containing one were transformed into the mesoporous ZSM-5 type crystals in the presence of in-situ crosslinked styrene/divinylbenzene in the mesopores of templates.
2. Experimental

2.1. Synthesis of mesoporous ZSM-5

First, SBA-15 silicas and Ti containing SBA-15 were synthesized in the type of powder and thin film using tetraethylorthosilicate and amphiphilic PEO-PPO-PEO triblock copolymer (Pluronic P123). A supramolecular silica-surfactant assembly of MCM-41 was also prepared by the reported methods [6]. The pore volume of the mesoporous material was filled with styrene monomer/divinyl benzene and AIBN(2,2’-Azo-bis-isobutyronitrile) by the incipient-wetness technique. The crosslinked polymer was synthesized in the pores at 100 °C. During the polymerization of styrene, the monomer-containing sample was put in the sealed vial to avoid the evaporation of monomers. These mesoporous materials have been used as a starting material for the synthesis of mesoporous ZSM-5 crystals. TPAOH solution was impregnated on those mesoporous materials and the mole ratio of TPAOH/SiO₂ was fixed as 0.3. After evaporation of the water, the final mixture was transferred to a Teflon-coated autoclave for further reaction to crystallize ZSM-5 zeolites at 170 °C. Transformation of the amorphous walls of MCM-41, SBA-15 and Ti
containing SBA-15 into the ZSM-5 crystals proceeded at 170 °C for 24h in the presence of saturated steam. It is essential that water in the autoclave should not be in direct contact with the samples during the crystallization. The solid product was recovered by filtration after washing with distilled water and dried at 120 °C overnight. The polymer was removed from the as-synthesized material by calcinations in air at 550 °C for 5h.
2.2. Characterization and Catalytic activity

XRD patterns were recorded on Phillips PW 1729 and Rigaku (miniflex) diffractometers using CuKα radiation. The morphologies of the samples were examined by TEM (Phillips CM-220) and SEM (Hitachi S-4300). N₂ adsorption and desorption isotherms were determined on a Micrometrics ASAP 2000 sorptometer at –196 °C. The samples were outgassed under 10⁻⁵ torr at 200 °C prior to the measurement.

The catalytic epoxidation was tested to characterize the catalytic performance of prepared Ti containing mesoporous ZSM-5 samples. The oxidation of α-pinene by tert-butyl hydroperoxide was performed using a batch-type reactor at room temperature. The conversion was determined by GC using a capillary column (HP-5 crosslinked 5% PHME Siloxane 30m×0.32×0.25µm Film Thickness).
Fig. 1. Chematic representation for the transformation of mesoporous materials into mesoporous ZSM-5 after formation of crosslinked polymers in the pore channels. Produced mesoporous ZSM-5 has bimodal micro/mesoscopic pores and it is readily obtained in the type of thin film, monolith as well as powder.
3. Results and Discussion

The successful incorporation of the mesopores within ZSM-5 type crystals could be performed by the synthesis method as shown schematically in Fig. 1.

The polymer chains present in the pores of mesoporous materials could remain firm during the high temperature crystallization of silicalite and TS-1.

Fig. 2(A-C) displays the powder XRD patterns of calcined mesoporous silicalites and TS-1. In the wide angle region, a series of peaks up to near $2\theta = 24^\circ$ becomes sharper and prominent with the crystallization time. The appearance of XRD peaks for microporous ZSM-5 as well as mesophase suggests that the amorphous silica/titania walls of mesoporous template are progressively transformed to crystalline phase through the encapsulation of nano polymers in the crystals.

Transmission electron microscopy (TEM) images reveal the appreciable mesoscopic order of samples. TEM micrographs of silicalite and TS-1 crystallized at 170 °C (Fig. 3B, 3D) display the presence of mesopores penetrating the entire crystals. This mesopore
system was resulted from the packing of nanosized ZSM-5 crystals. The mesoporosity is not observed on the conventional microporous TS-1 crystal as shown in the same Figure 3C.

Syntheses of related materials with bimodal micro/mesoscopic pores in the form of thin film have been demonstrated. The Ti containing SBA-15 sol was also prepared using amphiphilic triblock copolymer and it was coated on the porous silica surfaces. Consequently, micro/mesoporous TS-1 film could be formed and the mesoporosities penetrating the whole zeolite crystals are observed on the TEM image of samples.

In addition, mesoporous ZSM-5 monolith can be readily produced using Ti-SBA-15 sol and polyurethane sponge having connected macropore system as templates.
Fig. 2. XRD patterns of (A) mesoporous silicalite powder prepared using Ti-containing SBA-15 (B) from silica SBA-15, and (C) from MCM-41.
Fig. 3. TEM images of the calcined materials: (A) SBA-15 used as a starting material, (B) mesoporous silicalite powders obtained from siliceous SBA-15, (C) microporous TS-1, and (D) mesoporous TS-1 crystals.
Fig. 4. SEM photographs of (A) mesoporous silicalite powders obtained from siliceous SBA-15, (B) enlargement of photograph (A), (C) microporous ZSM-5 powders, and (D) mesoporous TS-1 crystals. SEM images are showing the top surface of mesoporous silicalite crystal films deposited on the matrix (E) and that of pure microporous ZSM-5 film(F).
SEM photographs of mesoporous silicalite and TS-1 show that each crystal exhibits the typical shape of ZSM-5 zeolite, and then it consists of very small aggregates (Fig. 4A, 4B, 4D). TS-1 in the coated layer showed the same morphologies as the mesostructured TS-1 powders as shown in Fig. 4E.

To analyze the pore geometry and structure, Brunauer-Emmett-Teller (BET) analysis was performed to measure the N₂ adsorption-desorption isotherm. Figure 5 displays N₂ adsorption-desorption isotherms of calcined mesoporous silicalite and TS-1 powder, respectively. N₂ adsorption-desorption isotherms of calcined mesoporous ZSM-5 powder gave type IV adsorption isotherm behavior and the steep rises at low relative pressures and at relative pressures between 0.8 – 0.9, indicating the presence of both micropores and mesopores.

The calcined mesoporous silicalite powder obtained using SBA-15 as a template had a N₂ BET total surface of 450 – 530 m²/g and a pore volume of 0.6 – 1.1 cm³/g. The mesopore surface areas are in the range of 190 – 220 m²/g. The meso TS-1 samples have very high mesopore surface areas of in the range of 170 – 200 m²/g and mesopore volumes between 0.4 – 0.8 cm³/g. The size of mesopores in
ZSM-5 powder obtained from various SBA-15 materials was estimated to be approximately 13 nm (Fig. 5B).

The catalytic epoxidation of bulky organic olefin molecule was investigated to characterize the catalytic performance of prepared mesoporous TS-1 samples.

Fig. 5. Nitrogen adsorption-desorption isotherms for the calcined mesoporous silicalite powder (A, B), and TS-1 (C, D).
For comparison, microporous TS-1 was also prepared and tested as a catalyst. The amount of titanium in catalysts was almost same. The epoxidation of \( \alpha \)-pinene was performed at room temperature using a usual batch-type reactor. The mesoporous TS-1 zeolites become much more active than microporous TS-1 when the bulky olefine is used as a substrate. The oxidation of \( \alpha \)-pinene to \( \alpha \)-pineneoxide proceeded 10 times faster over mesoporous TS-1 catalyst than with conventional microporous TS-1. This mesostructured TS-1 catalyst has the volumes of 0.6cm\(^3\)/g mesopore and 0.2 cm\(^3\)/g micropores. Consequently, the difference in the reaction rates was attributed to the textural mesoporosity in mesoporous TS-1, allowing a better access of the bulky reagent molecules to the active sites.
4. Conclusions

In this work, a simple and general procedure has been developed for the syntheses of mesoporous zeolites with a mean pore size of 5-15 nm. The excellent catalytic properties of a series of the mesoporous ZSM-5 expand the area for the application of porous materials, and can be used in a number of commercial processes in the future. Furthermore, such materials with bimodal micro/mesoscopic pores would be useful for many potential applications, such as heterogeneous catalysts, supports, sensor and membrane in the type of powder, thin film or monolith, when the bulky reactant molecules are involved..
References


Chapter 2

Syntheses and Application of Silica Monolith with Bimodal Meso/Macroscopic Pore Structure

1. Introduction

Microporous materials with pore diameters less than 1.5 nm (crystalline zeolites) have interest primarily, because of their material characteristics such as large internal surface area, unique pore structure, adsorption capacity and catalytic activity [1-3]. However, they have one limitation as catalysts. Their pore sizes are not efficient at processing large molecules of nanometer-scale sizes. Consequently, some recent research efforts have been paid to the synthesis of nanoporous or mesoporous materials with large pore sizes and uniform pore distribution [4-10]. These mesoporous materials obtained by the use of amphiphilic block copolymers would expand the areas for their applications, e.g. selective catalysts for large molecules and cooperative complexes for enantioselective catalytic
reactions.

The development of macroporous materials with pore sizes beyond 30nm has been reported using polystyrene latex spheres in a colloidal solution [4-5], and oil droplets in an oil-in-water emulsion [6]. Various methods were also introduced for the synthesis of macroporous materials using polymer gels [7], vesicles [8], foams [9], and bacteria [10] as templates.

Formation of porosity on two or three different length scales in an ordered fashion with interconnectivity between the pores and with hierarchical structure would be advantageous for a variety of applications. For catalytic applications, reactant molecules need to access readily the interior pore structure. It has been known that terminal epoxides are very important subclass for organic synthesis. As a consequence, the preparation of optically pure terminal epoxides has long stood as a most significant target for chiral building blocks. Chiral Co(III) salen complexes are very selective for the asymmetric hydrolysis of terminal epoxides [11]. These recently developed salen-based catalysts are appealing candidates for covalent attachment of homogeneous chiral salen ligands to the polymer or inorganic supports, and the corresponding immobilized salen derivatives were
shown to be efficient for the hydrolytic kinetic resolution (HKR) of terminal epoxides [12]. The heterogeneous catalysts offer practical advantages of the facile separation from reactants and products, as well as recovery and reuse.

Herein we report the synthesis of mesoporous silica monoliths having macropores inter-connected 3-dimensionally. Our strategy uses synthetic polystyrene spheres to produce a controlled three dimensionally interconnected macroporosity, nonionic block copolymer templates to produce mesoscale porosity in the silica walls. The interconnected macro pore structure of silica was an inverse replica of the polystyrene templates. The silica wall was built by mesoporous materials. Large and moldable meso/macro porous silica monolith could be obtained in centimeter scale. This hierarchically ordered macro/mesoporous silica could be applied as a support to anchor the chiral salen complexes for the enantioselective synthesis of epoxides.

We have synthesized the (PF$_6$) anion containing Co(III) polymeric salens immobilized on meso/macroporous silica and the asymmetric catalytic activities of these new catalysts have been investigated in the HKR of terminal epoxides.
2. Experimental

2.1 Materials Synthesis

The monodispersed poly styrene beads were synthesized by the emulsion polymerization method reported in the literature [13].

The synthesis of bimodal meso/macro porous silica composites was performed using the mix of polystyrene latex spheres as template and a silica sol containing surfactant in ethanol solvent as shown in Scheme1.

First, the calculated amounts of poly(ethylene oxide)-block-poly(propylene oxide)-block-(ethyl-ene oxide) (EO\textsubscript{20}PO\textsubscript{70}EO\textsubscript{20}, numbers in subscripts denote the molar ratios of each component) were dissolved in n-butanol/EtOH to make 35 wt% solutions. To prepare the prehydrolyzed inorganic precursor solution, tetraethoxy-orthosilane(TEOS) dissolved in n-butanol/EtOH was hydrolyzed in aqueous HCl solution. The molar ratio of TEOS : n-Butanol : Ethanol : H\textsubscript{2}O : HCl was 1 : 3 : 4 : 4 : 0.04.

Secondly, the silica sol-solution was added to the same volume of polystyrene latex spheres. The whole mixture was stirred at room temperature and it was centrifuged in polypropylene tube with 13,000
rpm. Then the mixture was dried slowly at room temperature for 5 days. The polystyrene latex spheres were removed by direct calcination at 550°C for 4 h in air. The heating rate was maintained 1°C/min.

**Scheme 1. Materials Synthesis**
2.2 Immobilization of chiral salen ligands on bimodal porous materials

The polymeric salen ligand was synthesized by using dimeric dialdehyde derivative(A), which was reported by Jacobs et. al [14]. A suspension of 5.38 g of 3-aminopropyl trimethoxysilane and 20g of meso/macro porous silica in 100 ml of toluene was heated to reflux with stirring. After heating for 12 hours, the powder sample (A) was filtered and washed with diethylether and toluene. The polymeric salen ligand immobilized on meso/macro porous silica (C) was obtained by the condensation reaction between dimeric dialdehyde derivative and (1R,2R)-(-)-1,2-diamino cyclohexane (B) in boiling ethanol solution as shown in Scheme2.

The Co(II) salen catalysts were obtained by the reaction between the salen ligands and hydrous cobalt (II) acetate in a boiling ethanol. For the synthesis of chiral Co(III)-(PF$_6$) salen catalysts immobilized meso/macro porous silica monolith (E), the cobalt(II) polymer salen (D) was treated with ferrocenium hexafluoro phosphate in acetonitrile under air. The mixture was washed with hexane to remove the side product, ferrocene. The catalytic activities were evaluated in the HKR of ($\pm$)ECH, 1,2-epoxybutane, propylene oxide and styrene oxide.
The general procedure for the HKR of epoxides follows the method as shown in the reported papers [13]. The conversion and ee% values were determined by chiral capillary GC using columns (CHIRALDEX (G-TA) and (A-TA), 20m × 0.32mm i.d. (Astech)).
Scheme 2. Immobilization of chiral salen ligands on bimodal porous materials
3. Results and Discussion

The centimeter-scale meso/macro silica monolith could be synthesized by using SBA-15 sol and polystyrene template to control the bulk shape and macropore structure. The particle size distribution of polystyrene latex was very narrow. The SEM image of polystyrene template sphere is shown in Fig. 1. These polystyrene latex particles are spherical in shape with uniform size of 550nm.

Fig. 1. SEM image of polystyrene latex sphere.
The bulk shape of meso/macroporous monolith was controlled and molded, according to the container. The shape of the calcined meso/macroporous silica monolith appears to replicate the centrifuge tube shape as shown in Fig. 2. Fig. 2 shows the transparent SBA-15 monolith obtained without addition of polystyrene beads. During the calcinations to remove the polystyrene templates densification of the silica network occurred, resulting in the shrinkage of the monolith.

Fig. 2. Photographs of different bulk shape of bimodal silica sample: SBA-15 monolith synthesized without PS templates (A), meso/ macro porous monoliths (B, C).
Sample | mol ratio (TEOS : Solvent)  
--- | ---  
A , B , C | 1 : 3  
D , E | 1 : 1

**Fig. 3.** SEM images of bimodal silica structure: (A) and (B) cross-section of the calcined monolith obtained from the mixture of n-butanol/ethanol solvent (n-Butanol : EtOH=1 : 3), (C) enlargement of (A), (D) low magnification of monolith sample obtained with decreasing solvent amount, (E) enlargement of (D).
Fig. 3 shows SEM images of the meso/macro porous silica monolith at different magnifications. Fig. 3A is the overall view of the cross-section of the monoliths and Fig. 3B is that of bulk surfaces. From these lower magnifications, it can be seen that large fractions of the calcined sample were highly ordered in three dimensions and the remaining portions exhibited uniform macro porosity interconnected through windows whose diameter is typically same as that of used polystyrene template.

The presence of ordered mesopores in the meso/macro porous silica monolith is supported by XRD, TEM and N₂ adsorption analysis.
Fig. 4. TEM image of meso/macro porous silica monolith

TEM image of monolith sample shown in Fig. 4 displays a hexagonal array of pore structure in large area. By visual inspection on the image, we measure the average diameter of the pore to be approximately 60 Å.
Fig. 5. XRD data of the calcined mesostructure

Fig. 5 shows typical XRD data of the calcined mesostructures. In Fig. 5, an intense peak at $2\Theta = 1.24 \pm 0.01^\circ$ is found and a broad peak in the $2\Theta$ region between 1.8 and 2.6$^\circ$ which corresponded to 100 main peak intensity and the overlap of two 110 and 200 peaks. The pore diameter, $D = 2d_{100}(\sqrt{3}\phi_{pore} / 2\pi)^{1/2}$, where $\phi_{pore}$ was 0.87, determined by the following N$_2$ adsorption-desorption measurement] was 69.8 Å which was quite similar to one measured by TEM image.
N₂ adsorption and desorption branch of mesoporous wall (Fig. 6) display steep changes with pressure, which is an indication of the presence of mesoporosity.
The trends in the activity and enantioselectivity of the synthesized the Co(III)-(PF₆) polymeric salens immobilized on meso/macro porous silica composites were examined for the HKR of epoxides. Table 1 shows the results obtained using the heterogeneous Co(III)-(PF₆) polymeric salens as catalysts.

**Table 1.** Enantioselective hydrolysis of terminal epoxides to diols on the Co(III)-(PF₆) salens immobilized over meso/macro porous composites.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Time(h)</th>
<th>Yield of epoxide(%)</th>
<th>ee% of epoxide</th>
<th>Yield of diol(%)</th>
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<tr>
<td>PO</td>
<td>6</td>
<td>43</td>
<td>99</td>
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<td>EB</td>
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<td>30</td>
<td>92</td>
<td>42</td>
</tr>
</tbody>
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1) PO; propylene oxide, EB; 1,2-epoxybutane ECH; epichlorohydrine, SO; styrene oxide
2) Epoxide; 10mmol, water; 0.55mmol, reaction temp.; 20°C
The Co(III)-(PF₆) polymeric salens immobilized on meso/macro porous silica composites showed excellent enantioselectivities with the substrates such as propylene oxide, 1,2-epoxybutane, epichlorohydrine, styrene oxide. The reaction using heterogenized Co(III)-(PF₆) catalysts exhibited the almost same enantioselectivity as homogeneous ones. It is so easy to isolate the immobilized salen catalysts from the product solution containing epoxide and diols. The immobilized catalyst was recoverable by simple filtration and solvent rinse.

The Co(III)-(PF₆) salen catalysts immobilized on meso/macro porous composites exhibited the same enantioselectivity up to 99% ee through the repeated use for fifth times in HKR of 1,2-epoxybutane.

The important feature in the HKR of ECH by using the Co(III)-(PF₆) salen catalysts immobilized on meso/macro SBA-15 is that no racemization is found not only during the distillation but also after attaining the highest ee% value of epoxides.
Fig. 7. The catalytic activities of Co(III)-(PF₆) salen catalysts immobilized on meso/macro porous silica in the asymmetric HKR of epoxides.
Fig. 8. The catalytic recyclabilities of heterogeneous Co(III)-(PF₆) salen catalysts on meso/macro porous silica asymmetric HKR of 1,2-epoxybutane
4. Conclusions

The synthesis and characterization of hierarchically ordered porous silica monoliths were examined in this study. Large silica monoliths could be obtained in centimeter scale from the mixture of monodispersed polystyrene beads and PEO-PPO-PEO/SBA-15 sol solutions. The adjacent macropores are interconnected through uniform-sized windows and the walls of these macrospheres consist of mesostructured pores. On the basis of asymmetric HKR of various epoxides, the new polymeric chiral (salen) complexes immobilized on the meso/macro porous silica monoliths obtained by the present procedure can be applied as effective heterogenized catalysts for the asymmetric reactions.
5. References

