Application of Mesoporous Silica Foam for Immobilization of Salen Complexes in Chiral Intermediates Synthesis

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A route to synthesize porous materials with a hierarchical micro/meso/macroscopic pore system was investigated. Meso/macroporous monolithic silica foams with a large pore size could be fabricated from a mixture of monodispersed PMMA beads and SBA-15, -16 sol solutions. The size, bulk shape and density of the mesoporous monolithic foam could be controlled by the container and the heat treatment temperature. Drying at temperatures higher than 300 °C resulted in an expansion of the SBA silica sol and its solidification to form the mesoporous foams. In contrast, only a dense silica monolith was obtained after full evaporation of the solvent at room temperature without releasing the foam structure in the monolithic body. A large fraction of macroporosity in three dimensions was formed in the monolith body, and the remaining silica walls exhibited uniform mesoporosity. Hydrolytic and phenolic ring-opening of epoxides were performed successfully using chiral (salen)Co-BF₃ complex-immobilized catalysts in the packed bed of a continuous flow system. Very high catalytic activity with desirable enantioselectivity was obtained in asymmetric catalysis.

Keywords: Monolith, Mesoporous silica, Foam, SBA-16, Enantioselectivity

Introduction

Microporous zeolitic materials with pore diameters less than 1.0 nm have attracted considerable interest in the field of adsorption and catalysis owing to their high surface area, unique pore structure and hydrothermal stability.^{1–3} However, their pore sizes are not efficient for processes involving large molecules. Consequently, some recent research on the synthesis of mesoporous materials with large pore sizes and uniform pore size distribution has been conducted.4-11 Nanostructured porous materials continue to attract significant research interest and have had a great impact in many applications, including catalysis, sorption, and separation.¹² Mesoporous materials with a pore diameter in the range of 2-10 nm may be suitable for a wide range of applications in enantioselective catalytic reactions to synthesize valuable medical substances.^{13–16} The large surface areas of porous materials can be used efficiently to anchor the active metal complexes of a large size through covalent bonding, and the large mesopore channels may allow the easy diffusion of reactants to these active sites for catalysis. The formation of porosity on two or three different length scales in an ordered manner with interconnectivity between the pores and with a hierarchical structure would be advantageous for a variety of applications. For catalytic applications, reactant molecules need to access readily the interior pore structure. Hierarchical materials containing both interconnected macroporous and mesoporous structures have enhanced properties compared to single-sized pore materials due to increased mass transport through the pore channels with a high specific surface area on the molecular levels. Obviously, significant advances in the

physico chemical properties of these materials can be expected if crystalline zeolites can be incorporated into the mesoporous frameworks.

Many researches were focused on the production of optically pure products due the increasing demand of such drugs to be administered in an optically pure form. The syntheses of optically pure chemicals have significant potential. Terminal epoxides are one of the important subclasses for organic synthesis. As a consequence, the preparation of optically pure terminal epoxides has been a significant target for the synthesis of chiral building-block in the pharmaceutical industry. The catalytic ring opening reaction provides a practical manner to prepare stereo chemically-enriched terminal epoxides. Several systems based on the chiral cobalt-salen complexes are quite efficient in the highly enantioselective synthesis of chiral epoxides by hydrolytic kinetic resolution (HKR). Typically, HKR of racemic terminal epoxides with water catalyzed by a chiral Co(III) salen complex may provide highly enantioriched epoxides and 1,2-diols. A recent study reported that [Co(salen)]-type complexes bearing transition-metal salts or BF₃ exhibited good enantioselectivity and reactivity for the HKR of racemic terminal oxiranes in the synthesis of chiral atenolol.¹⁷ From a practical synthetic point of view, phenol derivatives are appealing candidates as nucleophiles for the ring opening of racemic (±)-ephichlorohydrine ((±)ECH) providing direct access to enantiopure α-aryloxy alcohols using chiral cobalt-salen complexes.^{18,19} These recently developed salen-based catalysts are appealing candidates for the attachment of homogeneous chiral salen ligands to the inorganic supports, and the corresponding immobilized salen derivatives have been shown to be efficient for the phenolic kinetic

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resolution (PKR) of terminal epoxides.²⁰ Heterogeneous catalysts offer the practical advantages of the facile separation from reactants and products, as well as recovery and reuse. Considerable effort has been devoted not only to the development of active catalysts but also to finding ways to enable repeated use.^{21–24} This is particularly important for chiral catalysts, which are normally more expensive than achiral catalysts. These recently developed chiral salen-based catalysts are appealing candidates for the development of new methods for the recycling of chiral catalysts. Therefore, the present study focused on the development of optically active catalysts desirable for repeated use without any treatment after the reaction.

In this study, a mesoporous monolithic silica foam was newly fabricated from SBA sols. A large meso/macroporous silica monolith with the shape of the mold was synthesized on the centimeter scale. The foam-type silica monolith composites with three-dimensional macropore channels also could be obtained from a mixture of polymethylmetacrylate/SBA (PMMA/SBA) silica sol. The PMMA/SBA silica sol was expanded and solidified to a foam structure at high temperatures. After removing the PMMA polymer beads, a mesoporous silica foam remained. Large fractions of macroporosity in three dimensions were formed in the monolith body, and the remaining silica walls exhibited uniform mesoporosity. The micro/meso/macroporous silica monolith could be also fabricated from the MFI zeolite/SBA sol mixture by expansion into a foam structure. These porous supports were used to anchor the (BF₃) containing chiral Co(III) salens, and they were packed in the tube for use as a catalyst in the continuous flow type packed bed reactor system. The asymmetric catalytic activities of these catalysts were investigated in the HKR and PKR of ECH. This hierarchically-ordered macro/mesoporous silica was quite useful for anchoring bulky chiral catalysts, such as salen complexes. Based on the asymmetric HKR and PKR reactions performed in this study, the meso/macroporous silica monolithic foams can be applied as effective supports for the enantioselective synthesis of chiral compounds.

Experimental

Materials Synthesis. The synthesis of mesoporous silica foam was performed basically using a silica sol containing a surfactant in ethanol (EtOH) solvent. Before the foaming step at high temperatures, PMMA spheres or zeolite powders were added to the as-synthesized SBA-16 sol. First, the calculated amount of (ethylene oxide)106-(propylene oxide)70-(ethylene oxide)₁₀₆ (Pluronic F-127, numbers in subscripts denote the molar ratios of each component, Aldrich) was dissolved in EtOH. To prepare the prehydrolyzed inorganic precursor solution, tetraethoxy orthosilicate (TEOS, Aldrich) dissolved in EtOH was hydrolyzed in an aqueous hydrochloric acid (HCl) solution. The TEOS:F-127:ethanol:water:HCl molar ratio was 1:0.011:10.1:12:0.24. This SBA-16 sol was concentrated by evaporating the solvent until the volume of the sol mixture was reduced to one-third compared with the starting volume. At this time, PMMA spheres or MFI zeolite powders were added to the viscous silica sol-solution. The monodisperse PMMA spheres with mean diameters of 30 µm (TAFTIC TM FH-S series; for use of Light diffuser) were purchased from Toyobo Co. MFI type zeolite was treated with a diluted HF solution to produce mesopores in the microporous crystals. The resulting mixture was stirred at room temperature and then kept at 300 °C to allow self-expansion during solidification of the sol into the gel foam. Scheme 1 presents the



Scheme 1. Procedure for the fabrication of monolithic mesoporous silica foams.

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typical procedure to fabricate the mesoporous silica foam. The PMMA spheres and F-127 surfactant in the silica foam were removed by direct calcination at 600 °C for 4 h in air. The heating rate was maintained 1 °C/min. In addition, a SBA-15 sol was also prepared using P-123 (Aldrich, 98%) as a surfactant. **Immobilization of Chiral Salen Catalyst on Bimodal Porous Materials.** Anhydrous aluminum chloride (Aldrich, 98%) was dissolved in dried methanol. The monolithic silica foam was added to that solution. The aluminum chloride loadings used were 10, 20, and 30 wt% (Al basis) compared with the silica support. The solvent was evaporated and the recovered solid sample was calcined at 600 °C for 3 h in air.

For the synthesis of chiral Co(III)-(BF₃) salen, (R,R)-(-)-N, N'-bis(3,5-di-tert-butyl-salicylidene)-1,2-cyclo-hexane diamino cobalt (II) (Aldrich, 98%) was oxidized in air for 4 h in the presence of methylene chloride (MC) and BF₃·2H₂O (Co(II) salen:BF₃·2H₂O mole ratio = 1:1) at room temperature. The mixture was concentrated to dryness. Scheme 2 presents the immobilization method to obtain the catalyst and photographs of the silica foams for the fresh and catalyst loaded foams. The heterogenized chiral Co salen catalysts were packed in a stainless steel column (inner diameter 2 cm × length 15 cm), and this fixed bed type reactor was adopted to examine the catalytic activities in the HKR and PKR reaction of terminal epoxides. The reactants were circulated by a pump, and the inside pressure could be controlled up to 20 atm. In a representative reaction of (±)ECH (Aldrich, 98%) and phenol, a mixture of tert-butyl methyl ether (TBME; 150 ml, Aldrich) as a solvent, (±)ECH (9 g) and phenol (4.2 g) were circulated by pump through the reactor bed packed with the salen immobilized catalyst (3.4 g) at room temperature. The conversion and enantiomeric excess percentage (ee%) values were determined by GC using the chiral capillary columns (CHIRALDEX [G-TA] and [A-TA] columns, 20 m × 0.32 mm i.d., Astech, USA).

Characterization of Materials. The mesostructures of the inorganic composites were characterized by X-ray diffraction (XRD; DMAX 2500, Rigaku, Tokyo, Japan). In addition, transmission electron microscopy (TEM; Phillips CM-220, The Netherlands) was performed to examine the pore structures of the purely mesoporous or meso/macroporous materials. The morphologies of the samples were examined by scanning electron microscopy (SEM; S-4200, Hitachi, Japan). The N₂ adsorption and desorption isotherms were determined on a Micrometrics sorptometer (ASAP 2000, Micrometrics, Norcross, GA, USA) at –196 °C. The samples were outgassed under 10⁻⁵ torr at 200 °C prior to the measurement. The particle size distributions of the original polymer beads were determined by SEM.

Results and Discussion

The centimeter-scale mesoporous monolithic silica foam could be fabricated using SBA-15 or SBA-16 sol, which was obtained from a pure SBA sol or in conjunction with PMMA beads and Zeolite powder to control the bulk shape and macropore structure. Figure 1 shows a SEM image of the PMMA beads used as a template. The silica sol hydrolyzed in the presence of Pluronic F-127 (for SBA-16) was mixed with the template polymer spheres or MFI zeolite during heat



Scheme 2. Immobilization of chiral Co salen catalyst on the support and packing in the tube reactor for use in the continuous flow type reaction system.

treatment for foaming. After complete drying and removal of the polymer beads by calcination, the macro/mesoporous silica materials were fabricated with macroporous channels of different sizes inside the sample, depending on the amount of PMMA template added. For fabrication of the micro/ meso/macroporous silica monolith foam, a mixture of fresh H-type MFI zeolite powder and SBA sol was expanded and solidified into a foam structure. In this study, however, the HF treated mesoporous MFI zeolite was incorporated to increase the mesoporosity in the resulting silica foam. The formation of mesopores in MFI zeolite was confirmed by TEM (Figure 1(e)) and BET analysis (Figure 1(f)).

The size, density, and bulk shape of the mesoporous monolithic foam could be controlled, according to the container and the heat treatment temperature (Figure 2). At high drying temperatures, *e.g.*, 300 °C, the SBA silica sol was expanded and solidified to make the mesoporous foams. In contrast, the dense silica monolith was obtained after full evaporation of the solvent at room temperature. In this case, no foam structure was found in the monolithic body. Figure 2 shows the



Figure 1. SEM images of 30 µm PMMA beads (a), fresh MFI zeolite (b), HF treated mesoporous MFI zeolite (c) used as additives. TEM image of fresh MFI zeolite (d), HF-treated MFI zeolite (e), and BET result for HF treated MFI zeolite (f).



Figure 2. Photographs of the mesoporous silica foams: (a) left: pure SBA-16 foam; middle: MFI zeolite added one; right: PMMA bead added one; (b) fresh mesoporous SBA-16 foam, and (c) chiral salen complex anchored SBA-16 foam, (d) the sample (c) in MC solvent for the leaching test, and (e) fixed bed-type reaction system.

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shape of the calcined silica monolith foam made by replicating the shape of tube mold. The cylindrical shape of the silica monolith was obtained on the centimeter-scale (Figure 2(a)).

After immobilization of the chiral salen complexes with a BF_3 group on the Al-doped silica foam support, the color of the support turned to black indicating that they had been anchored (Figure 2(c)). The homogeneous salen catalyst adhered strongly to the support surfaces after the washing of the physically adsorbed complexes, without extraction in the organic polar solvents (Figure 2(d)). These heterogeneous chiral Co(III)-(BF₃) salen catalysts were packed in the tube reactor for use in the continuous flow type packed bed reactor system. Figure 2(e) shows the fixed bed reaction system used in this study.

Figure 3 presents the cross-sectional SEM images of silica monoliths obtained from the SBA-16 sol and monodispersed PMMA spheres. After calcination, the incorporated PMMA polymer beads were burned out and solid mesoporous silica remained. The large fractions of macroporosity in three dimensions were observed for the meso/macro composite fabricated from the PMMA/SBA-16 sol mixture (Figure 3(a)). When a large amount of PMMA was introduced, the remaining silica walls exhibited uniform mesoporosity, interconnected through windows, whose vacant void portion typically had the same shape as the starting PMMA template (Figure 3(b)). Figure 3 shows the similar form shapes of the silica monolith composites. Those samples displayed interconnected threedimensional macropore channels. When the silica sol and MFI zeolite were mixed, they were also expanded into the form structure and combined (Figure 3(d)).

The presence of mesopores in the silica foams was confirmed by XRD, TEM, and N_2 adsorption analysis. A TEM image of the monolith sample shown in Figure 4 showed a three-dimensional hexagonal array of pore structures for the silica foam synthesized from the SBA-15 sol containing the P-123 surfactant. However, a disordered mesopore structure was observed for the calcined silica foam sample synthesized from the SBA-16 sol but the mesoporosity throughout the whole silica foams was observed.

Figure 5 shows the XRD patterns of meso/macroporous SBA-15 and SBA-16 made by a sol–gel process. In the XRD pattern, SBA-16 sample shows an intense diffraction peak for the (1 0 0) plane. This might be due to the formation of a disordered pore structure. In Figure 5(b), an intense peak at 1.2° (2 θ) was observed with weak peaks in the 2 θ region between 1.82° and 2.4° , which corresponded to the (1 0 0) main peak intensity and the overlap of two (1 1 0) and (2 0 0) peaks. This is typical for a SBA-15 mesostructure showing regular hexagonal pore channels. These XRD patterns correspond well to the results obtained by TEM, as shown in Figure 4.

Figure 6 shows the N_2 adsorption-desorption isotherms of calcined SBA-15 and -16 mesoporous silica foam; the pore size distribution is plotted in the inset. The N_2 adsorption–desorption isotherm of the calcined original SBA-15 showed significant changes with pressure, which is an indication of the presence of mesoporosity (Figure 6(a)). In contrast, as it is shown in Figure 6(b), the SBA-16 mesoporous foam sample showed hysteresis due to the cage-like mesopore channels with an ink-bottle neck.



Figure 3. SEM images of silica foams at low magnification: (a, b) foams from PMMA/SBA-16 sol (60 wt% PMMA), (c) pure SBA-16 foam, and (d) foam obtained from the MFI/SBA-16 sol mixture.



Figure 4. TEM images of the mesoporous silica foams: (a) mesoporous SBA-15 and (b) mesoporous SBA-16 foam.



Figure 5. XRD patterns of the calcined silica foams fabricated from the SBA-15 and SBA-16 sol solution.

The heterogenized chiral Co-salen complexes present on the surfaces of mesoporous SBA-16 were characterized by FT-IR spectroscopy (Figure 7). SBA-16 can supply sufficient vacant spaces to attach the very large (salen) complexes inside the pore spaces. The characteristic IR peaks for homogeneous salen were observed at 1535-1612 and 2958-2950 cm⁻¹ on the spectra. The peaks near 2950 cm⁻¹ are due to the absorption by two aromatic rings and $1535-1612 \text{ cm}^{-1}$ due to aliphatics such as cyclohexane and tert-butyl groups in the salen structure (Figure 7(a)). On the spectrum (B), the symmetric and asymmetric stretching vibration bands for SiO2 of SBA-16 are found at 1000 and 1100 cm⁻¹. However, the broad band near 3500 cm⁻¹ is for the absorption due to the water molecules or silanol OH groups present on the mesoporous support. The chiral (salen) cobalt (III) complex-anchored mesoporous SBA-16 (Figure 7(c)) showed similar absorption bands of the pure homogeneous chiral (salen) complex (Figure 7(a)).

The micro/meso/macroporous silica forms were used as a support to anchor the (BF₃) containing chiral Co(III) salens,

and they were packed in the tube for use as a catalyst. The trends in the activity and enantioselectivity of the Co(III)-(BF₃) salens immobilized on mesoporous silica foam were examined for the HKR and PKR reaction of ECH in the continuous flow type packed bed reactor system. Figure 8 shows the activities of the catalyst in the asymmetric HKR of ECH by water in the circulating flow type packed-bed reactor. The results show the change in ee% of the resolved ECH with the reaction time. The HKR of (\pm) ECH was particularly efficient in terms of both the enantioselectivity (ee% up to 98%) and fast reaction rate. The reaction rate in asymmetric catalysis decreased with increasing flow rates of the reactants through the packed reactor. The high loading of the salen catalyst on the support exhibited higher activity, but a dilution of the reactants by a large amount of solvent resulted in a low reaction rate. For the effect of aluminum (Al) contents in SBA support, higher reaction rates were observed, when the increasing concentration of active sites was allowed on the same amount of supports. The active site means the chiral Co(III)-(BF₃) salen complex itself attached on the support. However the anchored amount of homogeneous salen complex was proportional to the contents of Al present on the supports, as shown in Scheme 2.²⁵ Aluminum chloride has oxidized during a heat treatment in air, and the Lewis acids generated by alumina oxide could combine the salen complexes strongly on the support. A higher local population of salen complexes on the same surface area was effective to accelerate the reaction rates and to increase the enantioselectivity.¹⁹ It is noteworthy to mention that Al showed no catalytic activity in this asymmetric reaction. The fixed bed-type insoluble heterogeneous Co(III)-(BF₃) salen catalysts could be applied easily in asymmetric catalysis with high efficiency.

The PKR reaction of (\pm) ECH by phenol was performed in the fixed bed reaction system and the results of the catalytic activity are summarized in Figure 9. As shown in this result, relatively high conversion was obtained using the catalyst with a high aluminum chloride loading under the same reaction conditions. In addition, the ee% of epoxide increased at a high aluminum chloride loading for the same reaction time and flow



Figure 6. N_2 adsorption–desorption isotherms: (a) calcined SBA-15 and (b) SBA-16 foam.



Figure 7. FT-IR spectra for: (a) homogeneous (BF_3) containing Co salen complex, (b) calcined SBA-16 foam, and (c) Co salen-immobilized SBA-16 foam.



Figure 8. Catalytic activities in the HKR of racemic ECH under different catalyst loadings and flow rates (THF solvent).



Figure 9. ee% change in ECH on the Co(III)-(BF₃) salen catalysts immobilized on mesoporous silica foam in the asymmetric PKR with phenol (flow rate: 50 mL/min, TBME solvent).

rate. The increase in ee% for the reactant ECH indicates that one optical epoxide was attacked selectively by nucleophile phenol on the chiral salen catalyst. Based on the observed results, a high loading of salen complexes on the support is essential to promote the reaction in terms of high enantioselectivity and conversion.

Table 1 lists the conversion and enantioselectivity obtained using different substrates with the catalyst and a 30 wt% AlCl₃

Table 1. PKR reaction of terminal epoxides to diols on the Co(III)-(BF₃) salens immobilized over meso/macroporous foam composites (the product yield is based on the reactant phenol derivatives).



Entry	Substrate (R)	Time (h)	Yield of product (%)	ee% of product
1	Н	7	84	98
2	Cl	10	76	96
3	CH ₃	11	82	98

loading, which was used to anchor the salen complexes onto the support. Both the electron-poor or -rich phenols reacted with (\pm)ECH enantioselectively to provide the corresponding α -aryloxy alcohols in good yield and high ee%. The introduction of Co(III)-(BF₃) salens in the meso/macroporous support was an essential factor for enhancing the catalytic activity and enantioselectivity. These salen-based catalysts showed a unique catalytic property to accelerate the kinetic resolutions in a highly efficient manner. No reaction has proceeded in the absence of the salen complexes.

The recyclability of the catalysts was examined in a PKR of (\pm) ECH using the 30 wt% Al-loaded heterogeneous catalyst. The catalyst was reused by simple washing with MC and THF after the reaction. The catalytic activity decreased slightly after 3 times reuse, indicating that some leaching of the salen catalyst from the support occurred during the reaction, as shown in Figure 10. No chemical isolation step of the salen catalyst was needed from the product solution in the heterogenized catalyst system.

The solvent plays a crucial role in this reaction. In the typical example, during the PKR reaction of (\pm) ECH with phenol or chlorophenol, the effects of polar and nonpolar solvents were examined, and nonpolar solvents, such as TBME was found to be the most suitable solvent, as illustrated in Figure 11.

The results obtained in this study highlight the importance to the asymmetric ring-opening of (±)ECH by HKR or PKR in pharmaceutical synthesis because the highly enantioenriched β -blockers can be synthesized easily in high yield using chiral cobalt-salen-type complexes. Further transformation into (*S*)-atenolol was accomplished using well-known simple methods (*i.e.*, by the addition of excess *i*PrNH₂ in the presence of H₂O at the reflux temperature, followed by treatment with aqueous NH₄OH). The heterogeneous catalyst could be recycled successfully without significant loss of activity and it is easy to isolate the immobilized salen catalysts from the product containing epoxide and α -aryloxy alcohols.



Figure 10. Catalytic activity of 30 wt% AlCl₃-loaded chiral salen catalyst in recycle reaction (flow rate: 50 mL/min, TBME solvent).



Figure 11. Effect of various solvents on the enantioselectivity in the PKR reaction of ECH by phenol and chlorophenol (highest ee% in the system, flow rate: 40 mL/min).

Conclusion

Porous materials with bimodal pore structures were synthesized, and their pore system was characterized by instrumental analysis and by comparing the catalytic activity at room temperature. The porous silica monolithic foams with a large pore size could be fabricated on the centimeter scale from a mixture of monodispersed PMMA beads or MFI zeolite in the SBA-16 silica sol. PMMA or zeolite/SBA silica sol was expanded and solidified into a foam structure at high temperature. In contrast, the dense silica monolith was obtained after full evaporation of the solvent at room temperature without releasing the foam structure in the monolithic body. After removing the PMMA polymer beads, the adjacent macropores were interconnected through the mesoporous silica walls as an expanded foam structure. In addition, the micro/meso/macroporous silica monolith could also be fabricated from the MFI zeolite/ SBA sol mixture by expansion into a foam structure. These porous supports were used to anchor the (BF₃)-containing chiral Co(III) salens, and they were packed in a tube for use as a catalyst in the continuous flow type packed bed reactor system. Based on the asymmetric HKR and PKR reactions, the chiral Co(III)-(BF3) salen immobilized on the meso/macro porous silica monolithic foams obtained in the present study can be applied as effective heterogenized catalysts for those reactions. The high catalytic properties of meso/ macroporous materials might expand the number of applications of porous materials, and can be used in a number of commercial processes in the future. Furthermore, such materials with bimodal meso/macroscopic pores would be useful for many potential applications, such as heterogeneous catalysts when bulky reactant molecules are involved.

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