Microporous Silica Membrane Synthesized on an Ordered Mesoporous Silica Sublayer

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Microporous inorganic membranes have attracted considerable attention for gas separation or membrane reactors due to their excellent thermal and chemical stability, good erosion resistance, and high-pressure stability compared to conventional polymeric membranes. The permeability of a microporous membrane is controlled by the pore volume fraction, whereas the selectivity is determined by the pore size and its distribution. Ordered microporous materials have high porosity and well-defined structure with narrow pore size distribution compared to amorphous materials. Several research groups have demonstrated that microporous membranes possess these promising separation characteristics over those based on Knudsen diffusion.[1−4] Among them, zeolites have unique properties for the crystalline structure that consists of a network of well-defined micropores.[5−7] For zeolite membranes, however, it is not easy to control pore size ranging from 1 to 10 nm with proper stability. Alternative strategies might be the use of a sol−gel method, which is easy to control for cases of micropores larger than the size of nitrogen. For example, unique ordered pore structures (hexagonal, cubic, etc.) can be prepared by polymerizing inorganic monomers into a self-organized structure that is formed by templating organic molecules.[8−12] The pore diameter of these materials can be controlled by the size of the templating molecules and ranges from 1 to 10 nm with a satisfactory level of porosity, which is suitable for handling molecules too large for the traditional zeolites. In particular, these structured materials can be synthesized as a thin film by a simple dip-coating or spin-casting procedure with sol−gel chemistry. Tsai et al.[13] reported a dual-layer microporous silica membrane with a surfactant-templated silica sublayer on the top of γ-alumina support. However, the formation of thin film with ordered pores that serves as a separation layer remains still as a challenge because the surfactant-templated coating solution tends to penetrate into and fill the support pores instead of forming the thin skin layer on the coarse support.[14] This is the primary thrust of the present study.

Here, we report the fabrication of dual-layered composite membranes with high permeability and selectivity onto a macroporous α-alumina support. The membrane preparation procedure is shown in Scheme 1. The α-alumina support was 2.1 and 1.9 mm in outer and inner diameters, respectively, and its porosity was 0.39 with the average pore diameter of 150 nm. First, we modified the macroporous α-alumina supports to possess appropriate hydrophobicity to prevent the hydrophilic silica sol from penetrating into the support during the subsequent dip-coating process. To do this, the support preheated at 200 °C for 48 h was immersed and quenched in 5% (v/v) octadecyltrichlorosilane (ODS) in toluene and dried after aging at 110 °C for 8 h. The ODS-modified macroporous support was then treated at room temperature for 2 h in 1% (v/v) trimethylchlorosilane in toluene and rinsed with dry toluene. By doing this, Si−Cl bonds were formed on the surface of the pretreated support, which eventually enhanced thermal stability with proper adhesion of the mesoporous silica layer onto the support. Then, continuous mesoporous silica films with large periodic cage and pore structures were synthesized on the pretreated hydrophobic α-alumina support by the dip-coating process. In the first coating process for the mesoporous silica layer, the coating solution was prepared by adding the templating ethanol (EtOH) solution of poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) triblock copolymers to silica sols, which were made by an acidic HCl-catalyzed sol−gel reaction of a silica precursor tetraethyl orthosilicate (TEOS). The triblock copolymers, $EO_{20}PO_{70}EO_{20}$ (Pluronic P123) and $EO_{106}PO_{70}EO_{106}$ (Pluronic F127), were used as templates for the mesoporous silica films with hexagonal and cubic pore arrangements, respectively, on the macroporous α-alumina substrates.[11,12] In the second coating for the microporous silica layer, the coating solution was prepared by the organic template approach; TEOS was used for the silica precursor and methacryloxypropyltrimethoxysilane (MPTMS) was added as an organic template.[3]

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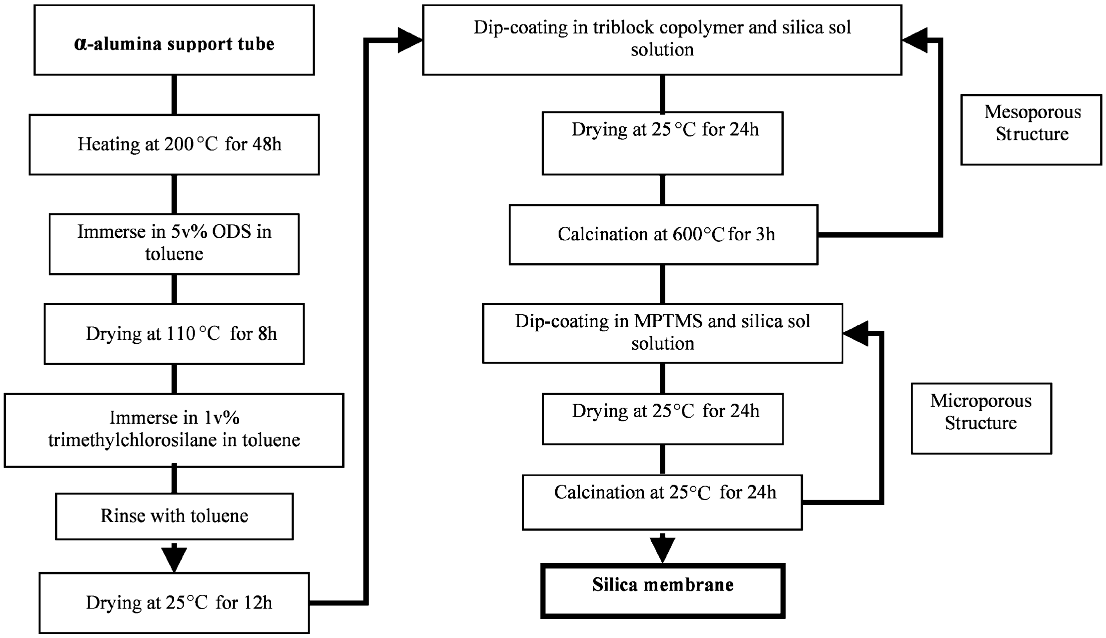
Scheme 1. Membrane Preparation Procedure



The N_2 adsorption/desorption isotherms, Brunauer–Emmett–Teller (BET) surface area, and XRD spectra showed that the mesoporous thin film had high pore volume (about 50–60%) and a well-defined structure. The pore size and BET surface area of the mesoporous silica ranged from 4 to 10 nm and from 350 to 400 m^2/g, respectively. In addition, the triblock copolymer templated silica showed high porosity and high surface area with narrow pore size distribution compared with the γ-alumina film as shown in Figure 1. The TEM images of the mesoporous silica in Figure 2 confirmed that the ordered mesostructures were preserved after calcination.

The SEM images of the film morphology are shown in Figure 3. When the support was not pretreated with ODS, the sol was able to penetrate into the macroporous support and the film morphology was poor as shown in Figure 3a. However, when the macroporous α-alumina support was modified with ODS, the silica sol was not able to penetrate the support due to the hydrophobic nature of the modified support, and the thin film was formed successfully as shown in Figure 3b. The film thickness ranged from 0.5 to 1.0 μm. As expected, the pretreatment considerably reduced unnecessary infiltration of the sol, which would in turn cause low permeability for the membrane separation processes. In

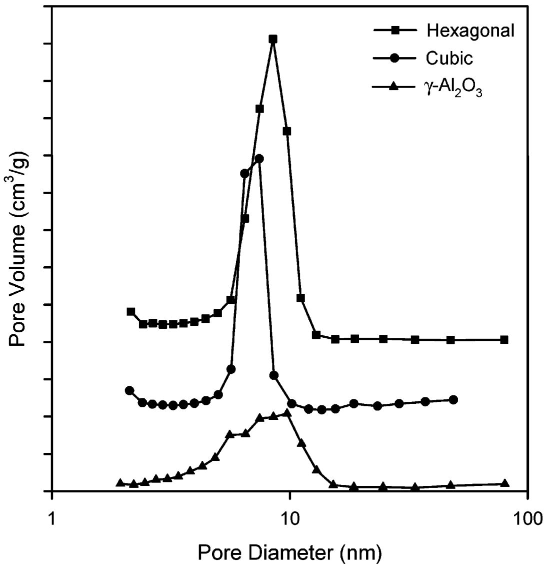


Figure 1. Pore size distribution obtained from the BJH model for the adsorption branch isotherm for the calcined mesoporous silica layers.

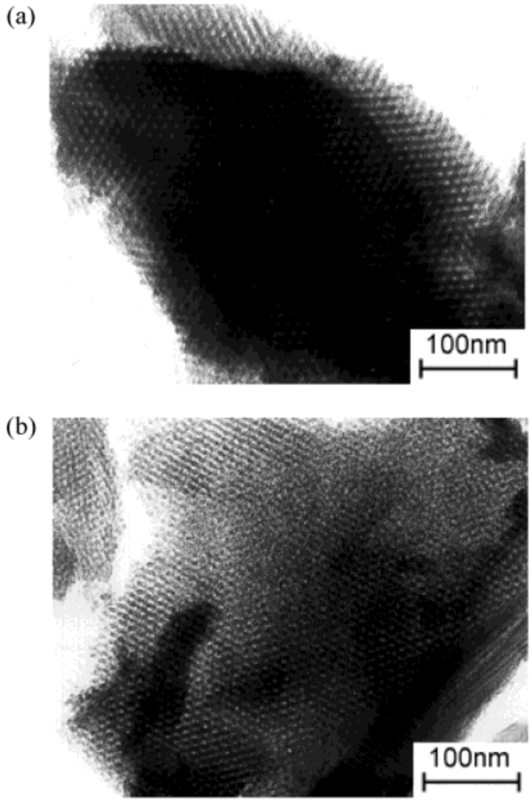


Figure 2. TEM images of the calcined silica films prepared using (a) $EO_{20}PO_{70}EO_{20}$ (hexagonal) and (b) $EO_{106}PO_{70}EO_{106}$ (cubic) triblock copolymers.

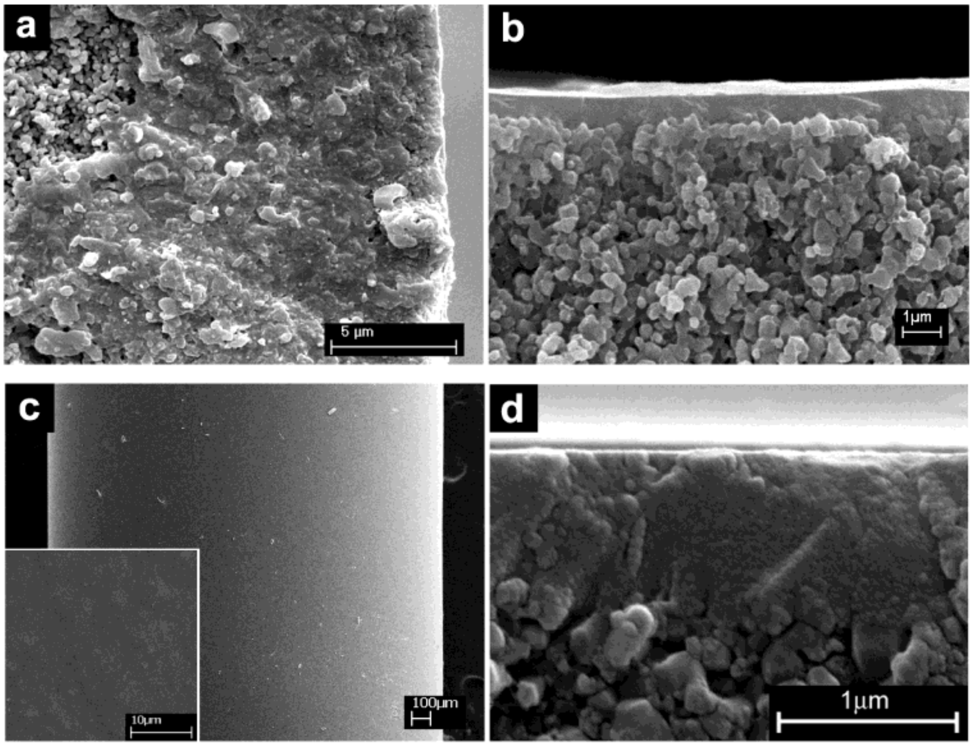


Figure 3. SEM images of the coated layers: (a) for the film coated on an α-alumina support without any pretreatment; (b) for the calcined cubic (Pluronic F127) mesoporous films coated on the pretreated hydrophobic α-alumina support; (c) for the MPTMS/TEOS sol coated layer on the sublayer (b); (d) for the cross section of the coated layer of (c). These images were taken after the separation test.

addition, the prepared thin film possessed highly favorable asymmetric structure, which enhances thermal stability with proper adhesion. The Si−Cl bonds on the surface of the pretreated support can be transformed back into Si−OH bonds if the surface is in contact with water molecules.[15] Figure 3c shows the surface of the microporous silica layer on the prepared hollow fiber membrane. Defects were greatly decreased by repeated film castings. The separative microporous silica layer is clearly visible with a thickness of 30−100 nm from Figure 3d.

Figure 4 shows the permeation behavior of the prepared membrane formed on the cubic sublayer for various gases. In this plot, we used three different membranes. The MPTMS membrane differs from the TEOS membrane in the addition of the organic template MPTMS and both were fabricated onto the mesoporous silica sublayer. Meanwhile, TEOS on a γ-Al_2O_3 membrane was fabricated onto an γ-alumina sublayer instead of a Pluronic-templated mesoporous sublayer. The permeation results indicate that the high porosity and ordered structure of the mesoporous sublayer greatly increased the gas permeance. Well-defined channels of the ordered mesoporous layer effectively shorten the paths for gas molecules to permeate through the membrane. Separation proceeded when the permeating molecule passed through the microporous skin layer. The permeance is decreased with an increase in the permeating molecule size over the Knudsen diffusion mechanism. The permeances are about 21 times higher for H_2 and 67 times higher for N_2 than those of the TEOS membrane without MPTMS prepared on the γ-alumina coated support. The selectivities of H_2 relative to N_2 for the MPTMS and TEOS membranes, both on the $EO_{106}PO_{70}EO_{106}$-templated sublayer are about 11.0 and 20.0, respectively, which are well above the ideal Knudsen limit of 3.74. The MPTMS membrane shows a similar permeation behavior of H_2 to the characteristics of zeolite membranes at 200 °C.

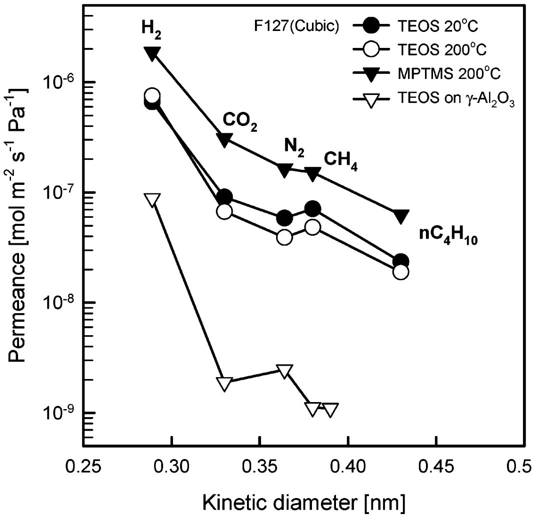


Figure 4. Permeance of the prepared membranes. Permeation proceeded at either 20 or 200 °C.

In summary, microporous silica membranes that were fabricated on the ordered mesoporous sublayer possessed very promising properties of high porosity and narrow pore size distribution. These membranes displayed very high permeance and selectivity for gas

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separation. The mesoporous membrane by itself can be used as ultrafiltration and pervaporation membranes and membrane reactors.

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