MFI-type zeolite membrane on hollow fiber substrate for hydrogen separation

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High performance MFI-type zeolite membranes on the outer surface of α-Al2O3 hollow fibers were synthesized by secondary growth method using pure silica sol without an organic template. X-ray diffraction was used to characterize the phase structure of both the seed layer and zeolite membrane. The morphologies of the seed layer and zeolite membrane were examined by scanning electron microscopy. The zeolite membrane achieved an extraordinary H2/CO2 separation factor of 10 with a high H2 permeance of 5.56 × 10−7 mol m−2 s−1 Pa−1 at 723 K.

MFI membrane, α-Al2O3 hollow fiber, H2 permeance, separation factor

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Zeolite membranes have attracted increasing interest because of their important potential applications in several areas [1]. MFI type zeolite membranes have potential for H2 separation [2]. In recent years, several research groups have synthesized good quality zeolite membranes without meso- and macroporous defects on disks [3] or tube substrates. However, reports of synthesis of good quality MFI-type zeolite membranes on hollow fibers are rare.

Liu et al. [4] reported the critical factors in synthesis of oriented MFI zeolite films. Seeding on the support is a crucial processing factor for synthesis of high-performance zeolite membranes [5–7]. Caro et al. [8] reported charging the support surface by pH control to achieve opposite charges on the seeds and support, which was then used for attachment by electrostatic attraction. This method makes it easy to obtain a uniform seed distribution, and continuous zeolite membranes can be prepared with high reproducibility.

In this paper, good quality MFI-type zeolite membranes were prepared on α-Al2O3 hollow fibers by the secondary growth method using pure silica sol without an organic template. We charged the support surface by pH control in a similar manner to Caro et al. [8]. We designed the synthesis strategy and method to avoid the template removal step. Firstly, nanosized silicalite powder was prepared by hydrothermal synthesis of a solution of 1 g of fumed silica, 5 mL (1 mol L−1) of TPAOH, and 0.07 g of NaOH at 120°C for 12 h. The crystals were purified by repeated centrifugation washes with deionized water. A stable seed sol was prepared from the silicalite powder (0.5 g), 14 mL of 0.5% hydroxy propylcellulose (HPC) (M = 100000 g mol−1) solution, and 33 mL of deionized water. The pH of this solution was adjusted from about 10 to 3–4 by addition of HNO3 (1 mol L−1). A continuous zeolite layer was coated on a porous α-Al2O3 hollow fiber by dip-coating the hollow fiber in the pH-adjusted seed solution. The supported seed layer was dried at 40°C for 2 d and calcined at 450°C for 8 h to remove the template. It was then placed in a template-free silicalite synthesis solution of 0.16 g of NaOH, 1 g of fumed silica, and 10.5 g of H2O at 180°C for 4 h, and then dried at 40°C for 2 d.

X-ray diffraction spectra of powders obtained from
crushed fibers after dip-coating and secondary growth are shown in Figure 1. Both the seed layer and zeolite membrane exhibited peaks characteristic of MFI-type zeolite between 5–25°, which indicates that the seed layer and membrane are pure MFI phase.

Scanning electron microscopy showed the outer diameter of the hollow fiber was about 1.8 mm, and the inner diameter was about 1.6 mm (Figure 2(a)). The micrographs of the surface of the seed layer (Figure 2(b)) and the zeolite membrane (Figure 2(c)) showed a uniform seed layer was obtained by dip-coating, and the grains after secondary growth were intergrown. As seen in micrograph (d), the zeolite membrane was about 3 μm thick.

The Al and Si concentrations on the surface of the zeolite membrane were analyzed by energy dispersive X-ray spectrometry (EDX). The zeolite membrane had an Al/Si ratio of 0.031, which is slightly lower than that reported by Pan et al. [9].

In single gas permeation tests, the sweep gas (He) flow rate was 15 cm³ min⁻¹ and the feed flow rate was 23 cm³ min⁻¹. The permselectivity of H₂/SF₆ and H₂/n-C₄H₁₀ were 152 and 125 (Table 1), respectively, at 298 K. These results are much larger than their Knudsen values of 8.54 and 5.38, and indicate the zeolite membrane is good quality. Furthermore, the permselectivity of H₂ over CO₂ was about 5.4 at 298 K. At 473 K this reduced to about 5.2, which is still larger than the Kudsen selectivity. These results show that the gas permeation is dominated by a molecular sieving mechanism for the zeolite membranes.

Figure 3 shows the temperature dependency of gas permeance for the MFI-type zeolite membrane at 298–723 K. In the separation of H₂/CO₂ mixtures, the total feed flow rate was 45 cm³ min⁻¹ and the He sweep flow rate was 33.5 cm³ min⁻¹. At 298 K, the MFI membrane was selective toward CO₂ and had low H₂ permeance because the preferentially adsorbed CO₂ limited the access of H₂ molecules to the zeolite pores. As the temperature increased, the H₂ permeance increased and the CO₂ permeance decreased until the membrane transitioned from being CO₂-selective to H₂-selective at about 380 K. The flux of H₂ was about 5.56×10⁻⁷ mol m⁻² s⁻¹ Pa⁻¹ at 723 K, which is larger than flux of H₂ on tube substrate [10], and the separation factor of H₂ over CO₂ was about 10 at 723 K.

In conclusion, pH control was used to create opposite charges on the seed and support, which allowed formation of a uniform seed layer. MFI type zeolite membranes were synthesized on α-Al₂O₃ hollow fiber with good reproducibility. Permselectivities of H₂/n-C₄H₁₀ and H₂/SF₆ on the MFI-type zeolite membrane were ideal at 125 and 152 at 298 K, which indicates the zeolite membranes are defect

Table 1 Permeance (×10⁻⁷ mol m⁻² s⁻¹ Pa⁻¹) of single gases on the zeolite membrane at 298 and 473 K

| Temperature(K) | H₂ | CO₂ | n-C₄H₁₀ | SF₆ | αH₂/n-C₄H₁₀ | αH₂/SF₆ |
|---------------|----|-----|---------|-----|-------------|---------|
| 298           | 6.38 | 1.18 | 0.051  | 0.042 | 125         | 152     |
| 473           | 7.23 | 1.39 | 0.087  | 0.075 | 83          | 96.4    |

Figure 2 Scanning electron micrographs of (a) α-Al₂O₃ hollow fiber, (b) calcined silicalite seed layer, (c) MFI-type zeolite membrane after secondary growth, (d) cross-section of the zeolite membrane.

Figure 1 X-ray diffraction patterns of calcined silicalite seed layer and zeolite membrane.

Figure 3 Permeance of an equimolar H₂/CO₂ mixture on MFI type zeolite membrane as a function of temperature.
free. The resultant zeolite membrane achieved an extraordinary \( H_2/CO_2 \) separation factor of 10 with a high \( H_2 \) permeance of \( 5.56 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1} \) at 723 K.

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