Preparation and Separation Performance of a TPAOH-Induced ANA Zeolite Membrane

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An ANA-type zeolite membrane with good H_2/C_3H_8 permselectivity has been prepared on an γ-Al_2O_3/α-Al_2O_3 support by in situ hydrothermal synthesis under the induction of tetrapropylammonium hydroxide (TPAOH).

In recent years, attempts to develop zeolite membranes for separation and catalytic application have intensified. Preparation methods such as in situ hydrothermal synthesis,[1,2] vapor phase transport[3] and secondary growth[4,5] have been developed for the synthesis of MFI, NaA, NaY, MOR and FER zeolite membranes. In the separation of small gaseous molecules, zeolite membranes with small pore size are used.[6,7] Inside analcime (ANA) zeolite, there are irregular channel (0.42×0.16 nm) of highly distorted 8-rings, with cross-sectional diameter less than that of CH_4. In 1996, Mimura et al.[8] reported the synthesis of an ANA membrane and its ion-sieve (Cs^+, Ag^+, Rb^+) ability. Here, we report the preparation, characterization and gas separation performance of an ANA zeolite membrane.

A self-made porous α-Al_2O_3 plate ($15 \times 15 \times 2$ mm) and an α-Al_2O_3 tube (O.D. 12 mm, I.D. 8 mm, length 100 mm, 0.2 μm pore radius, ca. 40% porosity) were used as support materials. Before hydrothermal synthesis, the α-Al_2O_3 tube was coated with a γ-Al_2O_3 layer of ca. 10 μm (pore size of around 3 nm) by sol-gel technique.[9] The synthesis mixture was prepared by mixing aluminum hydroxide, sodium hydroxide, water glass, TPAOH and deionized (D.I.) water. The molar composition of the gel was 1 TPAOH : 6 SiO_2 : 4 NaOH : 0.12 Al_2O_3 : 571 H_2O, where TPAOH was used as a template. The hydrothermal synthesis was carried out at 180 °C for 72 h in a stainless steel autoclave with the γ-Al_2O_3/α-Al_2O_3 tubes (two ends of which were sealed with Teflon tapes) being held vertically in the synthesis solution. For the α-Al_2O_3 plates, they were fastened on the aforesaid ceramic tube at different orientations. After synthesis, the composite membranes and ANA powder deposited at the bottom of the autoclave were rinsed with D.I. water to reach a pH of around 7. The ANA membrane was then dried overnight at 80 °C before heating (50 °C h^{-1}) to 500 °C for a calcination period of 6 h. The permeance of a gas through a tubular membrane generated in two cycles of hydrothermal synthesis was measured by a soap-film flowmeter under a pressure difference of 0.07 MPa and gas permselectivity is defined as permeance ratio of two gases.

The XRD patterns of the ANA powder and membranes prepared after one cycle of synthesis match those reported by Ferraris et al.[10] The results indicate that the membranes formed on α-Al_2O_3 plates exhibited a typical ANA zeolite structure. We also observed that a difference in plate orientation during synthesis makes no influence on the quality of the ANA membrane (Figure 1). According to the SEM results (Figure 2), the ANA zeolite crystallites that covered the surface of α-Al_2O_3 were with diameter within a 5–10 μm range; the thickness of the membrane was ca. 30 μm; and according to the results of EDX analysis, SiO_2/Al_2O_3 ratio was 4.13. In another words, the ANA zeolite membrane was pure and uniform in particle distribution.

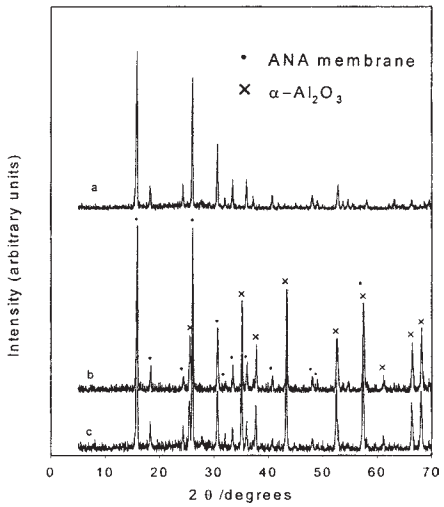

Figure 1. XRD patterns of (a) ANA powder generated from synthesis parent solution; (b) and (c) ANA zeolite membranes on two α-Al_2O_3 plates placed at different orientations during synthesis in the autoclave, respectively.

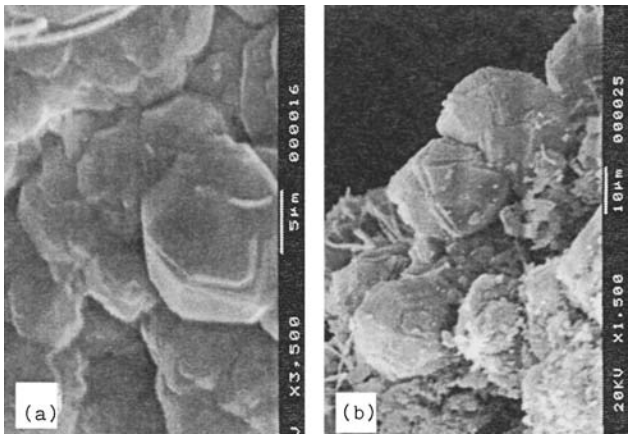

Figure 2. SEM images of ANA zeolite membrane on an α-Al_2O_3 plate after one cycle of synthesis; (a) top view (b) cross-section.

In order to evaluate the separation properties of the ANA zeolite membrane, the permeance of H_2, O_2, N_2, CH_4 and C_3H_8

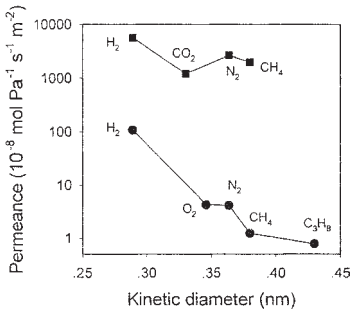

Figure 3. Relation between permeance and kinetic diameter; γ-Al_2O_3/α-Al_2O_3 support (■), ANA membrane (●).

was measured using the apparatus described previously.[11] Figure 3 illustrates the relationship between gas permeation and kinetic diameter. Compared to the case of a γ-Al_2O_3/α-Al_2O_3 tube, the permeance of H_2, N_2 and CH_4 through a supported ANA membrane decreased by two orders of magnitude, indicating the formation of a compact ANA membrane. One can observe that the permeance of H_2, O_2, N_2, CH_4 and C_3H_8 decreased with an increase in the molecular kinetic diameter. The results reveal a strong molecular sieving effect of the ANA zeolite membrane that is independent of molecular weight of gases. At room temperature, the permeance of O_2 (kinetic diameter, 0.346 nm) was 3.5 times higher than that of CH_4 (kinetic diameter, 0.38 nm), a result of reverse Knudsen diffusion mechanism. Meanwhile, the permselectivity of H_2/C_3H_8 observed over the as-synthesized ANA membrane was 138, significantly higher than the Knudsen diffusion value (4.69) of H_2/C_3H_8, as well as the results of H_2/*i*-C_4H_{10} (H_2/*i*-C_4H_{10} separation factor, 25) over a ZSM-5 membrane (pore size, 0.51 × 0.53 nm)[12] and H_2/*n*-C_4H_{10} (kinetic diameter, 0.43 nm; H_2/*n*-C_4H_{10} permselectivity, 106) over a NaA membrane.[13] The results indicate that the ANA zeolite membrane formed on γ-Al_2O_3/α-Al_2O_3 is of good quality. We observed that C_3H_8 diffusion through the membrane was in trace quantity, suggesting that the amount of intercrystalline pores in the ANA zeolite membrane is negligibly small.

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