

Synthesis and gas permeation properties of an NaA zeolite membrane

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A high quality NaA zeolite membrane, which shows a H₂/n-C₄H₁₀ permselectivity of 106, has been synthesized on a seeded α -Al₂O₃ support by a multistage synthesis method.

The synthesis of zeolite membranes and their application in separation and catalysis have attracted great interest in recent years.^{1,2} For gas separation, most studies have concentrated on MFI type (silicalite-1 and ZSM-5) zeolite membranes. Although high separation factors were obtained for mixtures of organic gases,^{3–6} MFI zeolite membranes do not show good separation performance for permanent gases or permanent gas/organic gas mixtures because of the large pore size and hydrophobic nature of the zeolite. Thus the investigation of zeolite membranes with small pore size has attracted much attention.^{7–9} NaA zeolite has a smaller pore size (0.41 nm) than that of MFI zeolite (*ca.* 0.55 nm). However, most studies on NaA zeolite membranes focused on the dehydration of liquid mixtures by pervaporation^{10,11} and few gas permeation results were reported.^{9,12} Furthermore, it was shown, from the gas permeation results,^{9,12} that the quality of these NaA zeolite membranes was poor. Here, a high quality NaA zeolite membrane has been synthesized on a seeded α -Al₂O₃ support by a multistage synthesis method.

A self-made porous α -Al₂O₃ disk (30 mm in diameter, 3 mm in thickness, 0.1–0.3 μ m pore radius, *ca.* 50% porosity) was used as the support. Before synthesis, one side of the support was coated with NaA zeolite crystals as nucleation seeds by dipping the support in a 0.5 wt% NaA zeolite suspension in a single step for 30 s. The 0.5 wt% NaA zeolite suspension was prepared by peptizing 0.5 g NaA zeolite in 100 ml deionized water. In order to form a thin and uniform NaA zeolite membrane on the support surface and to inhibit the formation of zeolite in the pores of the support, a uniformly sized NaA zeolite of dimensions *ca.* 1 μ m, larger than those of the pores of the support, was used as the seed. The synthesis mixture was prepared by mixing sodium aluminate, water glass, sodium hydroxide and water. The molar ratio of the resultant gel mixture was 3Na₂O : 2SiO₂ : Al₂O₃ : 200H₂O. The synthesis was carried out at 90 °C for 24 h in a stainless steel autoclave with the seeded support held vertically in the synthesis mixture by a Teflon holder. After the synthesis, the composite membrane was washed several times with water until the pH of the washings was neutral, then dried at 150 °C for 3 h. In order to obtain a high quality NaA zeolite membrane, the synthesis was repeated twice more (in all, a three-stage synthesis). The as-synthesized membrane was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and gas permeation studies. The permeances of the gases were measured at different temperatures by a soap-film flowmeter under a pressure difference of 0.10 MPa. The permselectivity of A/B is defined as the permeance ratio of gas A to gas B.

The XRD pattern of the as-synthesized membrane prepared by the three-stage synthesis is shown in Fig. 1. The diffraction pattern of the as-synthesized membrane is represented by the sum of the peaks of the α -Al₂O₃ support and the NaA zeolite, which indicated that the membrane formed on the α -Al₂O₃ support is an NaA zeolite membrane. The variation of the intensity of the diffraction patterns of the NaA zeolite is

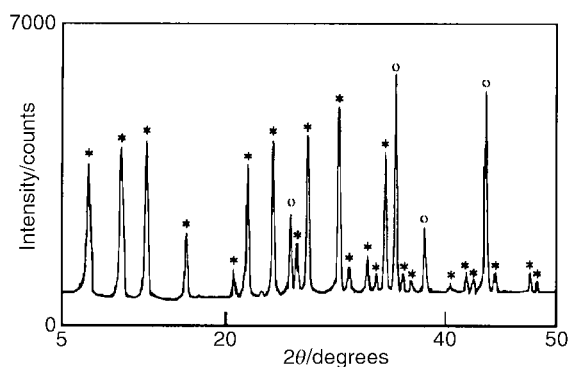


Fig. 1 XRD pattern of the NaA zeolite membrane: (○) α -Al₂O₃, (*) NaA zeolite.

possibly caused by the orientation of the zeolite crystals on the support surface. From the SEM images (Fig. 2), it can be seen that the surface of the α -Al₂O₃ support is completely covered with NaA zeolite crystals and the crystals are highly intergrown. A continuous membrane was formed on the support surface and the thickness of the zeolite membrane is *ca.* 18 μ m. In addition, the zeolite membrane remained firmly bonded to the support surface even after 15 min of vigorous ultrasonic vibration. However, XRD and SEM characterization can only indicate

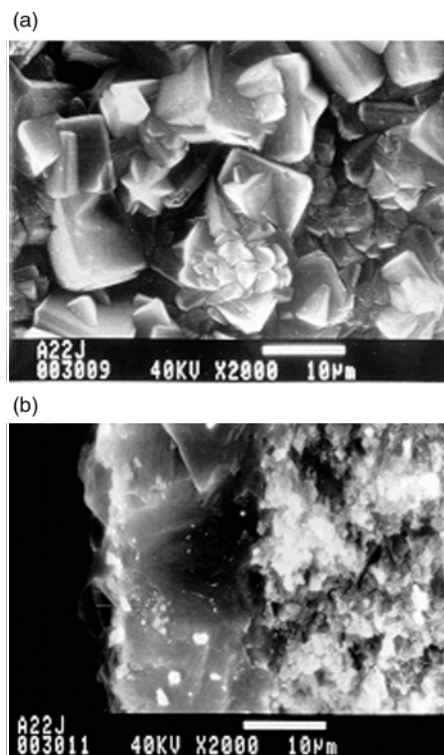


Fig. 2 SEM images of the NaA zeolite membrane: (a) top view, (b) cross-section.

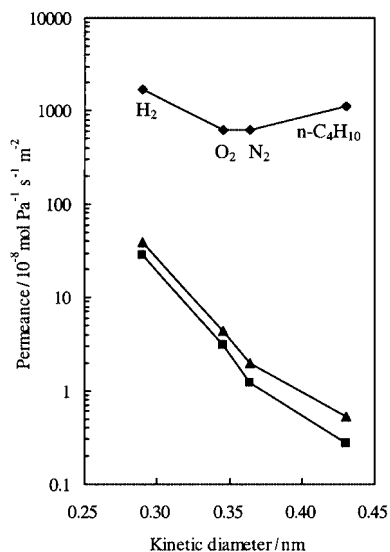


Fig. 3 Gas permeation properties of the seeded α -Al₂O₃ support (◆), the NaA zeolite membrane at 298 K (■) and the NaA zeolite membrane at 423 K (▲).

whether a continuous membrane is formed on the support, and can not confirm whether a defect-free zeolite membrane is formed. Such a property of the zeolite membrane can only be evaluated by gas permeation.⁵ Taking into the consideration the opening pore size of the NaA zeolite channels and the hydrophilic nature of the NaA zeolite, the permselectivities of H₂/n-C₄H₁₀ and O₂/N₂ were selected as the yardstick of the quality of the NaA zeolite membrane. Since the kinetic diameter of n-C₄H₁₀ (0.43 nm) is larger than the pore size of the NaA zeolite (0.41 nm), n-C₄H₁₀ should not permeate through a defect-free NaA zeolite membrane; the higher the permselectivity of H₂/n-C₄H₁₀, the more perfect is the NaA zeolite membrane. If the permselectivity of H₂/n-C₄H₁₀ is near to or smaller than the Knudsen diffusion ratio of 5.39, large defects must be present in the NaA zeolite membrane. Since the kinetic diameter of O₂ (0.346 nm) is smaller than that of N₂ (0.364 nm), the permeance of O₂ should be higher than that of N₂ through a defect-free NaA zeolite membrane which is the reverse of the Knudsen diffusion ratio of 0.96 for a mesoporous membrane. Fig. 3 shows the gas permeation results of the NaA zeolite membrane. The permeances of H₂, N₂ and O₂ of the supported NaA zeolite membrane decreased by two orders of magnitude compared with those of the α -Al₂O₃ support, which indicated that a compact zeolite membrane was formed on the porous α -Al₂O₃ support. With an increase of the molecular kinetic diameter, the permeances of the gases decreased, which showed

the molecular sieving effect of the NaA zeolite. At 298 K, the permeance of O₂ was 2.61 times higher than that of N₂, which is the reverse of that of the Knudsen diffusion ratio of 0.96. The permselectivity of H₂/n-C₄H₁₀ was 106, a value much higher than that of the Knudsen diffusion ratio of 5.39, which indicated that a high quality NaA zeolite membrane was formed on the support surface. Compared with the gas permeation results of NaA zeolite membranes in the literature,^{9,12} the NaA zeolite membrane synthesized in this study showed a very high H₂/n-C₄H₁₀ permselectivity. The reason for the formation of the high quality NaA zeolite membrane may arise from the use of uniformly sized seeds and is still under investigation. With an increase of the permeation temperature, the permeance of the gases increased. However, the permselectivity of H₂/n-C₄H₁₀ and O₂/N₂ at 423 K decreased to 73.2 and 2.22, respectively.

In conclusion, a high quality NaA zeolite membrane was successfully synthesized on a seeded α -Al₂O₃ support by a multistage synthesis method. The permeation of n-C₄H₁₀ indicated that the NaA zeolite membrane had intercrystalline pores larger than those of the NaA zeolite channels. The permeance of the NaA zeolite membrane was also relatively low. Methods for the preparation of high permeance or virtually perfect NaA zeolite membranes are under investigation.

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