

Synthesis and Separating Performance of SAPO-44 Zeolite Membrane

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Abstract: A defect-free SAPO-44 zeolite membrane firmly anchored the porous α -Al₂O₃ plate substrate was successfully synthesized. The separating results showed that the H₂/N₂ and H₂/CO permselectivities were higher than those of the corresponding Knudsen diffusion and the substrate, attaining 5.78 and 7.15 respectively.

Keywords: SAPO-44, zeolite membrane, gas separation.

Due to its high thermal and chemical stability, zeolite membranes have great potential application prospect, such as separation, catalysis, chemical sensors *etc.* Fewer type zeolite membranes with good separating performance have successfully been prepared in past decade¹⁻⁴. Therefore, study of new type zeolite membrane was important. SAPO-44 zeolite as a microporous small pore (~0.43 nm) silicon substituted aluminophosphate molecular sieve of chabazite structure, was firstly found by Union Carbide⁵. Because of the pore size closer to small molecule gases, synthesis of SAPO-44 zeolite membrane is of interest for separation and catalysis as membrane reactor. Synthesis of SAPO-44 zeolite membrane has been reported in the literature⁶, but the permeating performance of the membranes was not presented. This work reports synthesis of SAPO-44 zeolite membrane with good separating performance.

The porous α -Al₂O₃ substrate (the diameter of 24 mm, the thickness of 1.5 mm, and the porosity of 60 % as well as average pore size of 0.3 μ m) was polished with sandpaper and then pretreated in 12 mol/L sodium hydroxide for 12 h. After treatment, the substrate was dried at 120°C for 24 h and then transferred into the desiccator for further use. The synthesis mixture was used with the following molar composition of SiO₂: Al₂O₃: H₃PO₄: C₆H₇N: H₂O = 0.66:1.2:1.6:63. An uniform homogenous gel was prepared by firstly mixing aluminium, phosphoric acid and silicon sources in water and then adding the organic template. Here, we used boehmite (99.0 wt %, home-made by sol-gel method) as aluminium source and silica (87 wt %) as silicon source, and the organic template was cyclohexylamine. Then, the resulted mixture was vigorously stirred at room temperature

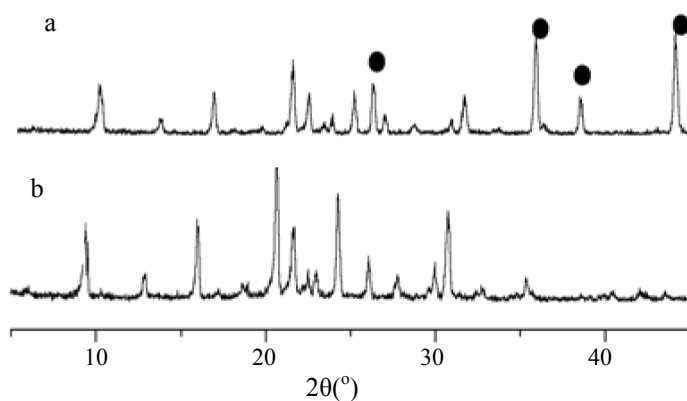
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and aged for 12 h. Finally, the treated substrate was vertically placed in a stainless steel autoclave and hydrothermally heated at 200°C for 24 h. After the ending, the substrate was washed repeatedly by deionized water and then transferred in permeating cell for drying at 120 °C with a 1 °C /min rising temperature for the overnight. Before removal of the template, the N₂ leak testing was performed on the dried and uncalcined membrane at room temperature. The uncalcined membrane was impervious to N₂ gas flow, indicating that it was defect-free. The template removal was operated at 600 °C with 0.2 °C /min rising temperature for the 6 h and then cooled to room temperature with 0.5 °C /min rising temperature.

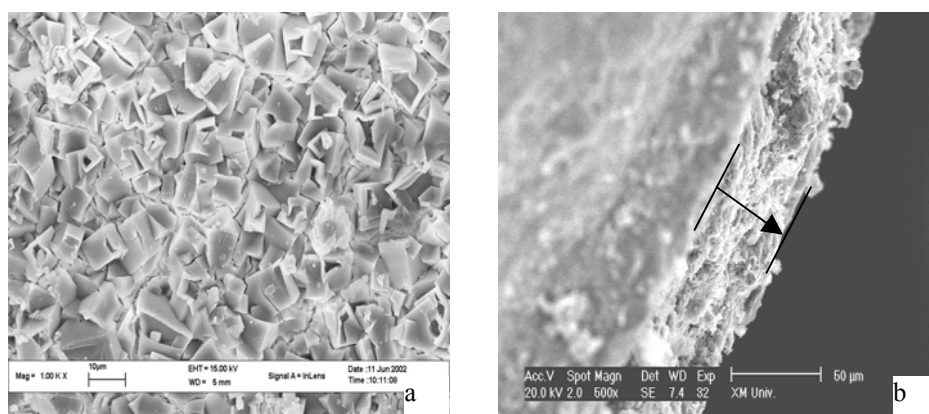
The formation of the zeolite membrane was confirmed by X-ray diffraction(XRD) using Rigaku Rotaflex D/MAX-C powder diffractometer with Cu K_α($\lambda=0.154$ nm) radiation at 40 kV and 30 mA. Electron micrographs were recorded with LEO-1530 (German) scanning electron microscope. Permeation tests were carried out on a home-made apparatus in our lab, which was previously described⁷.

Figure 1 showed XRD patterns of SAPO-44 zeolite membrane. The result indicated that the pure SAPO-44 zeolite crystals grew on the support in contrast to the peaks of SAPO-44 zeolite powder(see **Figure1-b**). SEM images of SAPO-44 zeolite membrane as shown in **Figure 2**, demonstrated that the SAPO-44 zeolite membrane consisted of highly intergrown crystals. SEM image of cross-section of zeolite membrane indicated that between the zeolite membrane and the substrate was well-knit (see **Figure 2-b**). The thickness of membrane was estimated about 40 μm .

Figure 1 XRD patterns of SAPO-44 zeolite composite membrane



a:SAPO-44 zeolite membrane, **b:** SAPO-44 zeolite powder(●: the peaks of $\alpha\text{-Al}_2\text{O}_3$ substrate)

Figure 2 SEM images of SAPO-44 zeolite membrane

a: Top view,

b: Cross-section view

The permeating results showed that the H_2/N_2 and H_2/CO permselectivities attained 5.78 and 7.15, higher than those of the corresponding Knudsen diffusion and the substrate, attaining, and the H_2 permeance was 1.40×10^{-7} mol/Pa·m²·s. N_2 and CO molecules have the same molecular weight, whereas the kinetic diameters are different, which are 0.36 nm and 0.37 nm respectively. If the diffusion is controlled by the Knudsen diffusion, the N_2/CO permselectivity is 1.00. The testing result showed that it was 1.23, suggesting that the pore channels of zeolite could partially affect the gas diffusion. The further investigation is underway.

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