

# NaA Zeolite Membrane with High Performance Synthesized by Vapor Phase Transformation Method

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NaA zeolite membrane was synthesized with high permeance on porous alumina substrate by the vapor phase transformation method. The membranes were characterized by XRD and SEM techniques. The XRD results showed that the membranes after the synthesis time of 24 h consisted of the pure NaA zeolite crystals. The SEM results showed that the membranes after the synthesis time of 48 h consisted of intergrown zeolite crystals. The H<sub>2</sub> permeance of the NaA zeolite membranes was higher than  $2.0 \times 10^{-6}$  mol/(Pa·m<sup>2</sup>·s), and the maximum of the gas H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> permselectivity was 7.15, which is higher than the corresponding Knudsen diffusion selectivity of which is 4.69.

**Keywords** NaA zeolite membrane, vapor phase transformation, synthesis, separation

## Introduction

Zeolite membranes, as a remarkable branch of inorganic membrane, have potential advantages in many applications such as catalysis and separation, chemical sensors, acoustic wave devices, and microelectronic devices due to their uniform pore size at the molecular level and resistance to high temperature.<sup>1-5</sup> For 10 years, many researchers have paid considerable attention to synthesis of zeolite membranes with high performance. Among the reported zeolite membranes, most attention was focused on synthesis of MFI-type zeolite membrane because it belongs to easily grown membrane on various supports and can be used in many catalytic reactions. As an important candidate membrane for gas separation, zeolite A membrane could be used to separate small molecule gases due to possessing the small pore (0.3—0.5 nm). Some studies on synthesis of zeolite A membranes from solution have been reported in literatures.<sup>6-13</sup> However, the reported NaA zeolite membranes usually have a good separation factor, but the permeance is too low for practical applications.<sup>6-10</sup> So, the developing trend of zeolite membrane is to synthesize thin membrane with high permeance and sustainable se-

lectivity. As to zeolite membrane, the vapor phase transformation method is available to synthesize thin zeolite membrane with high permeance. The objectives of the present study were to synthesize NaA zeolite membrane with high permeance on porous alumina substrates by the vapor phase transformation method.

## Experimental

The  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> substrates, with 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  $\mu$ m, were polished and then pretreated in 12 mol/L sodium hydroxide solution for 12 h. After treatment, the substrates were dried at 120 °C for 24 h and then put in the desiccator for further use. A nutrient solution with a molar composition of 15Na<sub>2</sub>O:4SiO<sub>2</sub>:1Al<sub>2</sub>O<sub>3</sub>:800H<sub>2</sub>O was prepared by first dissolving Al(OH)<sub>3</sub> in a 6 mol/L NaOH solution and then introducing a SiO<sub>2</sub> sol (25 wt% in water) under intense stirring at room temperature. The resulted solution above was aged for 24 h at room temperature. One side of substrates was dip-coated there times in synthesis solution at room temperature for drying and then put horizontally above the water by a support contained in Teflon vessels. The crystallized temperature was adjusted at 90 °C and treated for different time. After the synthesis, the as-synthesized membranes were washed several times by deionized water until neutral and dried at room temperature. Before measurements, the substrates or membrane discs were *in situ* heated in the permeation cell from room temperature to 120 °C with a raising rate of 1 °C/min and kept at that temperature for 12 h to get rid of water molecules in the pores. The permeance of the membrane was measured by a soap-film flowmeter under the pressure difference of 0.1 MPa at 25 °C. The permselectivity of A/B is defined as the permeance ratio of the gas A and the gas B. The formation of zeolite mem-

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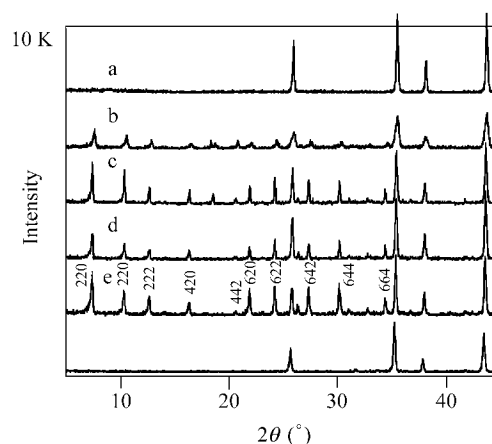
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branes was confirmed by X-ray diffraction (XRD) using a Rigaku Rotaflex D/MAX-C powder diffractometer with  $\text{Cu K}\alpha$  ( $\lambda = 0.154 \text{ nm}$ ) radiation, with operation condition at 40 kV and 30 mA. Electron micrographs were recorded with XL-30 ESEM TMP (PHILIPS) scanning electron microscope.

## Results and discussion

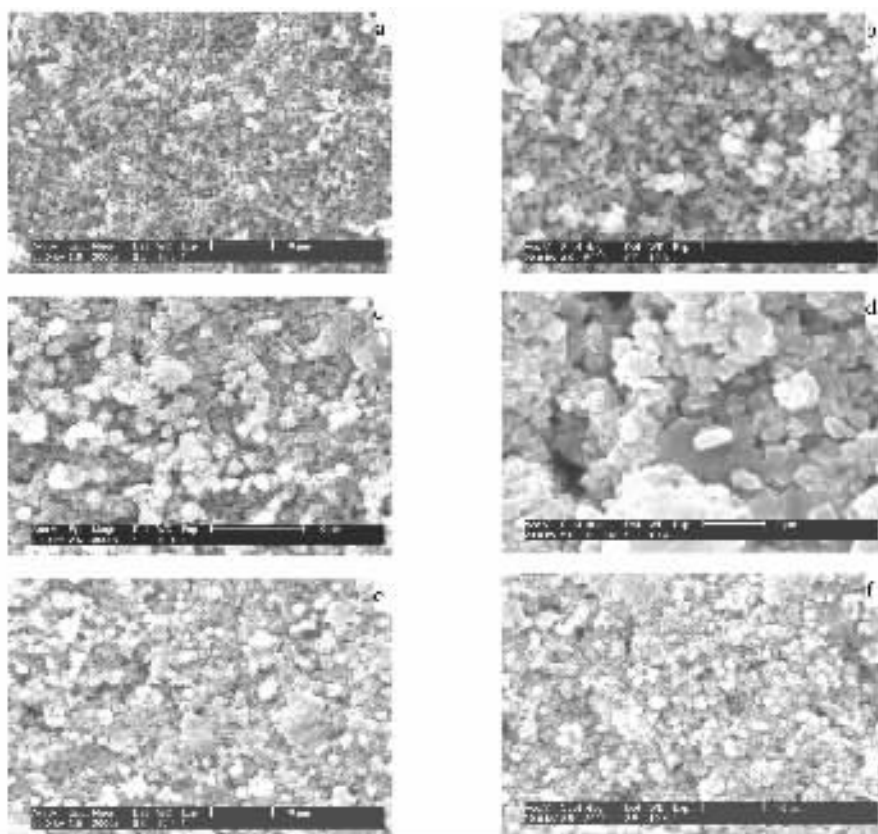
Fig. 1 shows the XRD patterns of the zeolite membranes synthesized by the vapor phase transformation method along with the synthesis time. From the patterns, it can be seen that no zeolites existed on the substrate when the synthesis time was 12 h. Along with the synthesis time to prolong to 24 h, the peaks of NaA zeolites appeared on the patterns, indicating that then the zeolite crystals grew on the substrate. When the synthesis time increased to 24 h, the intensity of the peaks of zeolite clearly enhanced and after 24 h it varied indistinctively, suggested that the gel on the substrate completely crystallized after the synthesis time of 24 h. Most of the peaks of zeolite appear on the patterns, suggesting that the zeolite crystals grew in all directions.

The SEM images of the zeolite membranes along with the synthesis time are shown in Fig. 2. With increasing of the synthesis time, the integrity of the membranes was clearly improved. After the synthesis time prolonged to 36



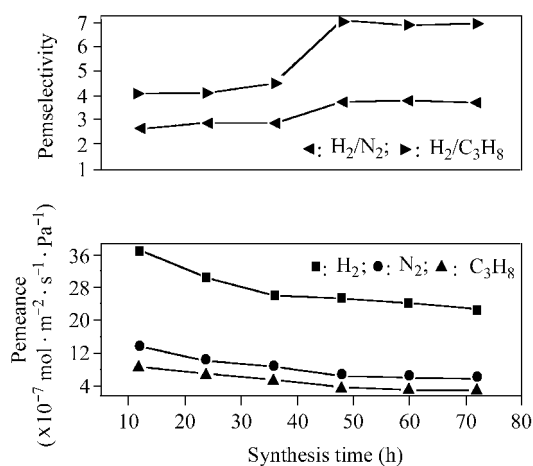
**Fig. 1** XRD patterns of the NaA zeolite membranes along with the synthesis time. a, 12 h; b, 24 h; c, 36 h; d, 48 h; e, 72 h; f,  $\alpha\text{-Al}_2\text{O}_3$  substrate; NaA zeolite No. 226; syn-gony: cube; unit cell parameter:  $a = b = c = 2.461 \text{ nm}$ ;  $\alpha = \beta = \gamma = 90.00^\circ$ .

h, the compact and continuous zeolite membrane grew on the substrates and the crystals constituting the membranes were uniform. In the case of Fig. 2e f, the intergrowth of the crystals was clearly visible. The integrity of the membrane may be further improved by the repeated synthesis, but the thinner membrane would be preferred in order to reduce the possibility of cracking during the drying. Therefore, all the membranes were synthesized once.



**Fig. 2** SEM images of the NaA zeolite membranes along with the synthesis time. a, 20 h; b, 24 h; c, 36 h; d, 48 h; e, 60 h; f, 72 h.

All the permeation tests were carried out at room temperature with single gases. The permeance and permselectivities of the NaA zeolite membranes as a function of the synthesis time are shown in Fig. 3. Along with increasing of the synthesis time, the  $H_2$  permeance decreased, whereas the  $H_2/N_2$  permselectivity elevated until the synthesis time prolonged to 48 h. It was noticeable that the  $H_2$  permeance on the membranes was above  $2.0 \times 10^{-6} \text{ mol}/(\text{Pa} \cdot \text{m}^2 \cdot \text{s})$ , higher than that of those reports, such as  $1.0 \times 10^{-7} \text{ mol}/(\text{Pa} \cdot \text{m}^2 \cdot \text{s})$  reported by Ma *et al.*,<sup>6</sup> and Aoki *et al.*,<sup>7</sup>  $1.02 \times 10^{-7} \text{ mol}/(\text{Pa} \cdot \text{m}^2 \cdot \text{s})$  reported by Xu *et al.*,<sup>8,9</sup>  $1.4 \times 10^{-6} \text{ mol}/(\text{Pa} \cdot \text{m}^2 \cdot \text{s})$  reported by Chen *et al.*,<sup>13</sup> indicating that the membranes have good permeating performance. From the permselectivities of  $H_2/N_2$  and  $H_2/C_3H_8$  as showed in Fig. 3, it can be seen that the  $H_2/N_2$  permselectivity along with the synthesis time elevated appreciably, and the highest permselectivity was 3.84, close to the corresponding Knudsen diffusion selectivity of 3.74. However, the  $H_2/C_3H_8$  permselectivity increased from 4.14 to 7.15 when the synthesis time was prolonged from 12 h to 48 h. After the synthesis time of 48 h, the  $H_2/C_3H_8$  permselectivity attained a maximum of 7.14, higher than the corresponding Knudsen diffusion selectivity of 4.69, indicating that the NaA membranes after that were compact and continuous. However, the permeation of  $C_3H_8$  suggested that there existed some pinholes and large defects.



**Fig. 3** Permeance and permselectivities of the NaA zeolite membranes along with the synthesis time.

Compared with the gas permeation results of NaA zeolite membranes in the literatures,<sup>7-9,13</sup> the NaA zeolite membranes in this report showed a very high performance.

The  $H_2$  permeance was about 20 times larger than that of the literatures,<sup>7-9</sup> and about 2 times than that of the literature.<sup>13</sup> The lower permselectivity of the zeolite membranes in this work was ascribed to the trade-off relationship of the permeance and the permselectivity of the membranes. How to improve the permselectivity of zeolite membrane needs further investigation.

## Conclusion

Compact NaA zeolite membranes with high performance were synthesized on the porous substrates by vapor phase transformation method. The  $H_2$  permeance of the NaA zeolite membranes was higher than  $2.0 \times 10^{-6} \text{ mol}/(\text{Pa} \cdot \text{m}^2 \cdot \text{s})$ , and the maximum of the gas  $H_2/C_3H_8$  permselectivity was 7.15, which is higher than the corresponding Knudsen diffusion selectivity of 4.69, suggesting a potential application for industry. However, the integrity of zeolite membrane needs to be improved by the further investigation.

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