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# Novel synthesis of FAU-type zeolite membrane with high performance†

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**FAU-type zeolite membranes were synthesized by the vapor phase transformation (VPT) methods with or without prior seeding on the substrate, and it was revealed that the $CO_2/N_2$ selectivity of the seeded membrane is greater than that of the unseeded membrane.**

Since zeolites possess well defined micropores, considerable attention has been focused on the production of zeolite membranes which are capable of separating gases at high selectivities. Several methods for the preparation of zeolite membranes have been describe.[1–4] and fall into three different strategies. (1) the direct crystallization method, (2) the vapor phase transformation (VPT) method, (3) the secondary growth method involving prior seeding on the substrate surface. In the past, most of the zeolite membranes have been synthesized using the direct crystallization method, but the method usually failed to give compact zeolite membranes. Since the secondary growth method appeared, many valuable zeolite membranes have been sucessfully synthesized, such as the types LTA,[4] MFI,[5] FAU,[6] and so on. Therefore, the secondary growth method has been revealed to be a powerful one, and aroused great research interests in zeolite membranes. So far, only a few types of zeolite membranes have been synthesized by the VPT method, thereof including the LTA type[7] and the MFI type.[8] No other type of zeolite membrane has been prepared by this method. The purpose of this communication is to present the synthesis of the Y-type zeolite membranes by the VPT methods with and without prior seeding on the subtrates.

The channel synstem in the FAU-type structures is three dimensional with equidimensional chennels intersecting in a perpendicular fashion. The free aperture diameter of the channels is 0.74 nm in Y-type. Zeolite membranes of FAU-type may be of particular interest due to their high aluminum content, *i.e.* their hydrophilicity. As has been proved elsewhere,[9] the FAU-type membrane exhibits high performance for $CO_2/N_2$ separatation.

The porous $\alpha$-$Al_2O_3$ substrate (24 mm in diameter and 1.5 mm in thickness) with a porosity of 60% and an average pore size of 0.3 μm was polished with sandpaper, treated in an aqueous solution of sodium hydroxide (10 mol $L^{-1}$) for 12 h, dried at 120 °C for 24 h and then transferred into a desiccator for further use. The seeds with an average size of *ca.* 40 nm were prepared by a microwave synthesis method, as described in our previous report.[10] A dip-coating method was used for seeding. A suspension of the nanosized zeolite seeds (0.5 g) of in ethanol (100 mL) was ultrasonically treated for 30 min, and then, one side of the substrate was immersed in the suspension for 30 s. The coating procedure was repeated three times, and the resulting seeded substrate was dried at room temperature for 24 h. The zeolite membrance was synthsized as follows. Sodium hydroxide and silica sol (25 wt.%) were mixed with distilled water and the mixture was stirred at room temperature to give a clear solution. Then an aqueous solution of $Al_2(SO_4)_3$ was added dropwise with stirring at room temperature and the mixture was left to age at room temperature for 24 h. The molar composition of the mixture corresponds to 15 $SiO_2$ : 1 $Al_2O_3$ : 11 $Na_2O$ : 648 $H_2O$. The seeded side of the substrate was dipped in the solution for 30 s, and the procedure was repeated at least three times. After being dried in air at room temperature, the substrates was mounted on the support in a Teflon-lined stainless steel vessel containing distilled water, and then the vessel was sealed and heated at 100 °C for several days. After cooling down, the substrate was washed several times with deionized water until neutrality and dried at room temperature. The synthesis of the membrane on the unseeded substrate was performed according to a similar procedure.

The formation of zeolite membranes was confirmed by X-ray diffraction (XRD) using a Rigaku Rotaflex D/MAX-C powder diffractometer with Cu K$\alpha$ ($\lambda$ = 0.154 nm) radiation (40 kV and 30 mA). Electronic micrographs were recorded on a XL-30 ESEM TMP(PHILIPS) scanning electronic microscope. The Si/Al ratio was calculated with the formula $SiO_2/Al_2O_3 = (25.248 - a_o) \times 2/0.245$.

Fig. 1 shows the XRD patterns of the zeolite membranes synthesized on the unseeded and seeded substrates, together with the patterns of the NaY zeolite powder and the substrate. It can be seen that the patterns of the zeolite membranes are consistent with that of the zeolite powder, confirming that the synthesized zeolite membranes have the FAU-type structure. The $SiO_2/Al_2O_3$ ratios of the zeolite membranes on the unseeded and seeded substrates were calculated to be 4.1 and 4.8, respectively. The $SiO_2/Al_2O_3$ ratio of the nanosized NaY zeolite seeds is 5.2, suggesting that the large $SiO_2/Al_2O_3$ ratio of the zeolite membrane synthesized after seeding is likely to be ascribed to the high ratio of the seeds.

Fig. 2 shows the SEM images of the zeolite membranes. The membrane grown on the unseeded substrate covers most area of the substrate, but it clearly exists some large defects. On the contrary, the zeolite membrane grown on the seeded substrate shows a good integrity, and consists of highly intergrown zeolite crystals. These results verify that the seeds play an important role in the synthesis of zeolite membranes by promoting the growth of zeolite crystals on the substrate. The thickness of the zeolite membrane grown on

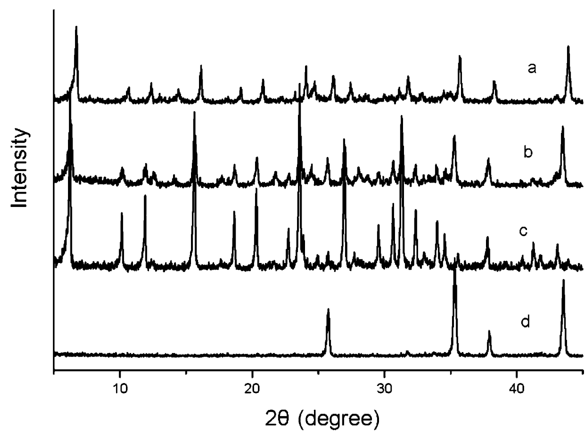


**Fig. 1** XRD patterns. (a) The zeolite membrane on the unseeded substrate, obtained by heating at 100 °C for 4 days; (b) the zeolite membrane on the seeded substrate, obtained by heating at 100 °C for 2 days; (c) the NaY zeolite powder (Si/Al = 2.6); (d) the substrate.

† Electronic supplementary information (ESI) available: Time dependence of the $CO_2$ and $N_2$ permeation. See http://www.rsc.org/suppdata/cc/b4/b405691d/

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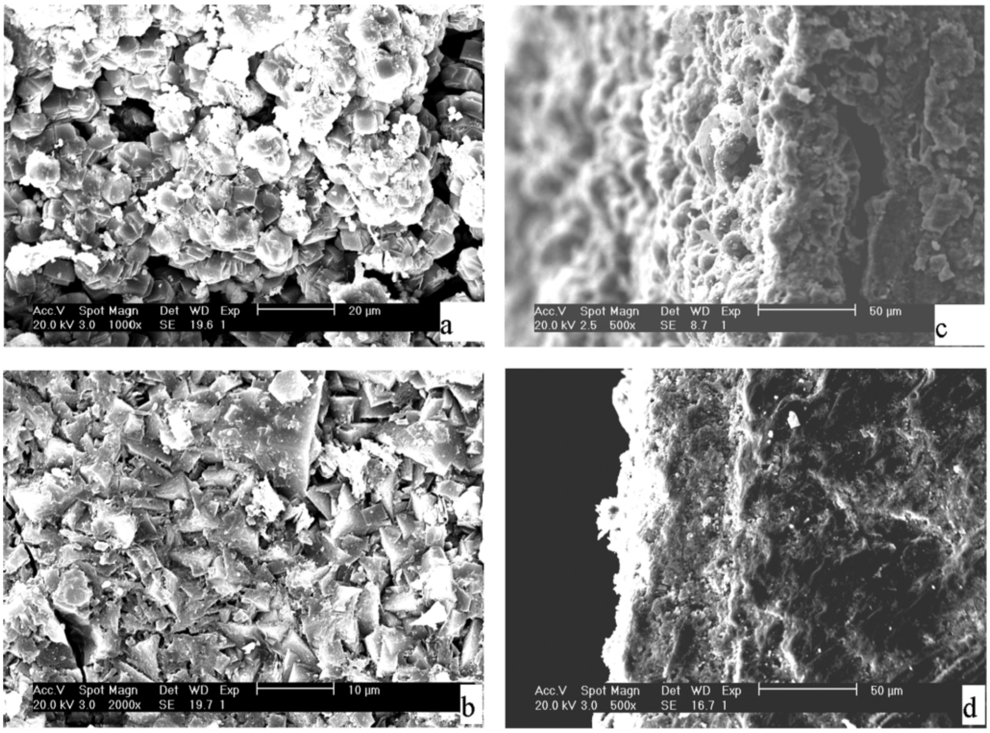


**Fig. 2** SEM images of zeolite membranes grown on the unseeded substrate (a, c) and the seeded substrate (b, d). (a, b) top view; (c, d) cross-section view.

the seeded substrate is *ca.* 50 μm, which is thicker than that of the zeolite membrane grown on the unseeded substrate (*ca.* 40 μm).

We used the $CO_2/N_2$ mixture (1 : 1, mole ratio) to evaluate the separation performance of the zeolite membranes. Before measurements, the membranes were heated *in situ* in the permeation cell from room temperature to 120 °C with a rising rate of 1 °C $min^{-1}$ and dried at that temperature for 12 h.

The gas separation measurements were carried out using the sweep gas method. The two sides of membrane were maintained under a pressure difference of 0.10 MPa, while helium was used as sweep gas in the permeating side, with a flow rate of 30 mL $min^{-1}$. The permeating side was maintained at atmosphere pressure and the permeating gas was monitored by on-line GC analysis.

The separation performance of zeolite membranes as the function of the permeation temperature is given in Fig. 3. All the data were collected at the steady state. As can be seen from the figure, the zeolite membrane formed on the unseeded substrate shows a poor separating ability, probably due to the presence of defects, which have been revealed by the SEM image. However, the zeolite membrane formed on the seeded substrate exhibits a good separation performance. At 25 °C, the selectivity of the $CO_2/N_2$ mixture through the zeolite membrane on the seeded substrate attains a maximum of 53.7, indicating that the membrane has a good integrity.

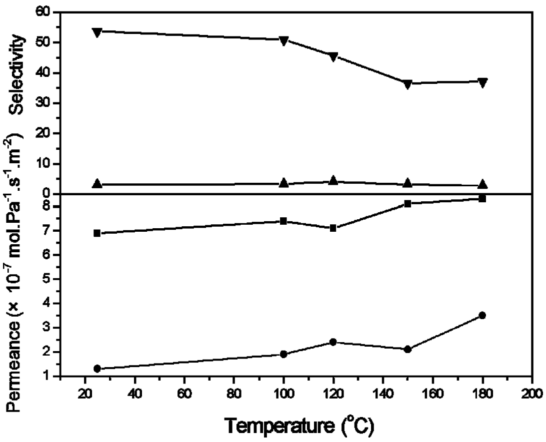


**Fig. 3** Temperature dependence of the $CO_2$ permeation (■, unseeded membrane; ●, seeded membrane) and the $CO_2/N_2$ separation selectivity (▲, unseeded membrane; ▼, seeded membrane).

In summary, we have successfully synthesized the Y-type zeolite membranes by the VPT method and its combination with prior seeding on the substrate. It has been shown that the latter method, a novel secondary growth method involving prior seeding and secondary VPT synthesis, can yield zeolite membranes with greater integrity and separation performance. The results should be of great interest with respect to the synthesis of zeolite membranes with good performance.

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