Preparation of NaA Zeolite Membrane with High Permeability by Using a Modified VPT Method

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A novel method was developed for the preparation of NaA zeolite membrane with high quality. The method consisted of two stages, i.e., preseeding and secondary growth, and the two stages were both performed under the condition of vapor-phase transformation (VPT).

Zeolite membranes have found versatile applications in the areas such as separation, catalysis, and sensor, in virtue of their uniform pore size at molecular level and large resistance to harsh environments.[1–5] The preparation of zeolite membranes with high performance is now attracting considerable attention. Reports concerning the preparation of zeolite membranes bring about mainly three different strategies: (1) direct crystallization; (2) vapor-phase transformation (VPT), and (3) secondary growth, i.e., preseeding followed by crystallization. The direct crystallization method has been most frequently employed in the preparation of zeolite membranes, it is, however, difficult to obtain compact membranes for many types of zeolites. The secondary growth method exhibits merit in the construction of compact thin zeolite membranes, and using this method, many valuable zeolite membranes, such as, A-type,[6] MFI-type,[7] FAU-type,[8] were successfully prepared. Since sophisticated arts were usually involved, the secondary growth method is hard to be diffusely adopted by researchers. The VPT method appears to be a promising way in the preparation of zeolite membranes, because of the fact that significant amount of nutrients is available for the growth of zeolite crystals over the surface of substrate. So far, few types of zeolite membranes, including LTA-type[9,10] and MFI-type,[11] were prepared by the VPT method. To obtain a zeolite membrane with high permselectivity at considerable permeance via the VPT method, improvements seem to be necessitated. In this short report, we presents a novel method that integrates the secondary growth and the VPT methods, i.e., the seeding and crystal growth are both performed under the VPT condition.

The substrate was a α-Al_2O_3 disc ($24 \times 1.5\,mm$) with a porosity of 60% and an average pore size of $0.3\,\mu m$. After being polished, the substrate was pretreated in a NaOH aqueous solution of $10\,mol\,L^{-1}$ for 12 h and dried at 120 °C for 24 h. A slip-coating procedure was employed in the formation of a film containing precursor species and a vapor-phase transformation one in the successive crystallization of the LTA seeds. The colloidal solution used in the slip-coating was prepared as follows. Initially, aluminium isopropoxide and tetramethylammonium hydroxide pentahydrate were dissolved in an aqueous solution of sodium hydroxide (0.4 g of sodium hydroxide dissolved in 70.6 mL of distilled water) under stirring at room temperature, to which an ethanol solution of tetraethylsilicate (27.8 g tetraethylsilicate dissolved in 115.0 mL of EtOH) was introduced. The mixture formed had a molar composition of $5SiO_2{:}1Al_2O_3{:}8(TPA)_2O{:}0.22Na_2O{:}400H_2O{:}200EtOH$ and was kept stirring for 4 h until a clear solution A was attained. Then, the solution A was transferred into a Teflon vessel and statically crystallized at 60 °C for 6 d, resulting in a transparent colloidal solution B. Next, the slip-casting procedure was performed by sliding one side of the substrate on the surface of the solution B and then drawing the substrate back. The process was allowed to repeat for several times until a thin film was formed on the substrate. Finally, the substrate was mounted vertically on a holder, embedded in a 40-mL Teflon vessel containing 20 mL of distilled water, and hydrothermally treated at 90 °C for 2 days. The as-obtained seeded substrate was employed for the subsequent step.

The nutrient solution for the secondary growth was prepared by dissolving $Al(OH)_3$ in 6 M NaOH aqueous solution, to which SiO_2 sol (25 wt % in water) was introduced under intense stirring at room temperature. The solution obtained had a molar composition of $15Na_2O{:}4SiO_2{:}1Al_2O_3{:}800H_2O$ and was aged for 24 h at room temperature. One side of the seeded substrate was dip-coated for three times in the nutrient solution. After that, the substrate was left at room temperature for drying and then put horizontally on the support fixed in a Teflon vessel containing 20 mL of distilled water. The crystallization was performed at 90 °C for 36 h, and the zeolite membrane formed was washed by distilled water for several times until neutrality and then dried at room temperature. The as-prepared zeolite membrane was subjected to the following characterizations.

X-ray diffraction (XRD) measurements were performed on a Rigaku Rotaflex D/MAX-C powder diffractometer with

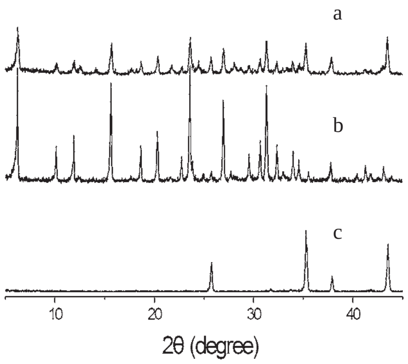

Figure 1. XRD patterns of NaA zeolite membrane grown on seeded substrate. a: NaA zeolite membrane; b: NaA zeolite powder; c: α-Al_2O_3 substrate.

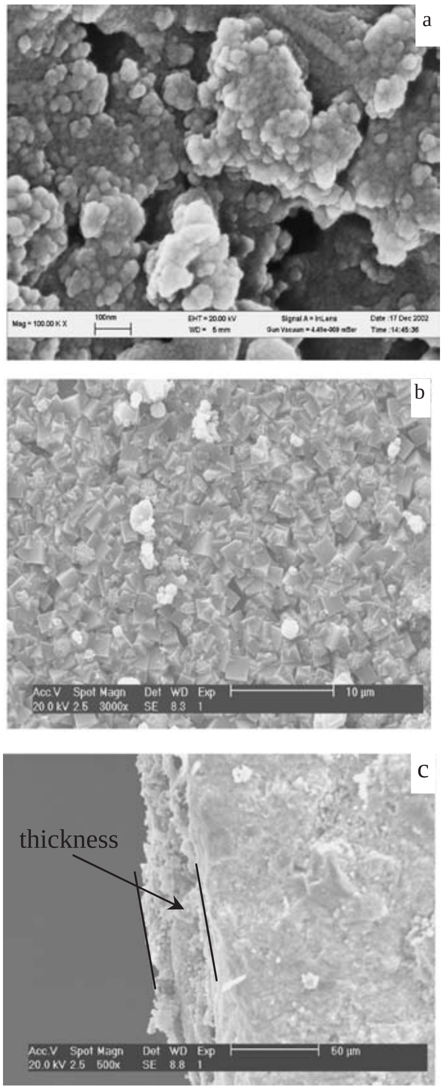

Figure 2. SEM micrographs of seeded substrate and NaA zeolite membrane. a) and b), top view (seeded substrate (a) and NaA zeolite membrane (b)); c: cross-section view (NaA zeolite membrane).

Cu Kα ($\lambda = 0.154$ nm) radiation, operated at 40 kV and 30 mA. Electron micrographs were recorded with a XL-30 ESEM TMP (PHILIPS) scanning electron microscope. Figure 1 shows the XRD patterns of the NaA zeolite membrane grown on the seeded substrate, the NaA zeolite powder, and the pure substrate. It can be concluded clearly that NaA zeolite film was formed over the substrate. Figure 2 shows the SEM micrographs of the seeded substrate and the NaA zeolite membrane grown on the seeded substrate. It can be found that the substrate is covered fully by a layer of seeds with an average size of ca. 60 nm (Figure 2a), and the zeolite membrane consisted of the uniform zeolite crystals with an average size of ca. 2 μm (Figure 2b). The thickness of the zeolite membrane is ca. 25 μm (Figure 2c).

The permeation tests were carried out on a home-made apparatus. Before measurements, the zeolite membrane was heated in situ in the permeation cell from room temperature to 120 °C with a rate of 1 °C/min and kept at that temperature for 12 h. 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 H_2 permeance on the prepared zeolite membrane was found to be 2.0×10^{-6} mol/Pa·m^2·s, which is slightly higher than that of 1.64×10^{-6} mol/Pa·m^2·s reported by Chen et al.[12] The H_2/N_2, H_2/CO, and H_2/C_3H_8 permselectivities were determined to be 3.81, 3.94, and 8.13, respectively, being higher than those of the corresponding Knudsen diffusion selectivities of 3.74, 3.74, and 4.69.

In summary, we have successfully prepared the NaA zeolite membranes via a novel method that integrate the secondary growth and the VPT ones. The zeolite membrane exhibited a better integrity and gas-separation performance. It is believed that the method developed in this paper would be also promising in the preparation of other types of zeolite membranes with good performances.

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