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Article

Synthesis and pervaporation performance of highly reproducible zeolite T membranes from clear solutions

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ABSTRACT

Zeolite T membranes with very good permeation performance were successfully synthesized on porous mullite supports by the secondary growth method with homemade microsized seeds from clear solutions. The influence of synthesis parameters such as the molar ratios of SiO_2/Al_2O_3 and H_2O/SiO_2, alkalinity, synthesis temperature, and crystallization time on membrane growth and permeation performance was investigated systematically. It is found that these parameters strongly affect the zeolite T growth and pervaporation performance of the membranes. Under the optimized synthesis conditions of $1SiO_2{:}0.015Al_2O_3{:}0.41(Na_2O{+}K_2O){:}30H_2O$, the crystallization time was shortened to 6 h at 423 K and a continuous and dense T-type zeolite layer as thin as 5 μm formed on the surface of the support. It significantly improved the membrane density and permselective properties. A permeation flux and separation factor of 4.20 kg/(m^2·h) and 7800, respectively, were obtained with the as-synthesized membrane for 10 wt% water-90 wt% *i*-propanol mixtures at 348 K. It also exhibited a very good pervaporation performance for water/ethanol mixtures separation. This high quality zeolite T membrane could be reproducibly prepared.

1. Introduction

Membrane separation is energy-efficient and many membranes have been developed for gas separation, catalytic membrane reactors, and pervaporation (PV) for liquid separation [1–3]. With a Si/Al ratio of 3–4, the intergrowth of erionite and offretite, and an effective pore size of 0.36 nm × 0.51 nm, zeolite T has both hydrophilic and fairly high acid-resistant properties [4–22]. Therefore, zeolite T membranes have great potential for applications in gas separation and liquid separation by PV. In 2003, Cui et al. [4] first reported a zeolite T membrane synthesized on seeded mullite supports by hydrothermal synthesis, showing excellent CO_2 separation performance. The membrane was as thick as 20 μm and showed good PV performance for dehydrating separation of water/organics mixtures such as water/*i*-propanol mixtures and catalytic membrane reactors of esterification reactions [4–7]. Although some reports have described the preparation and permeation performance of zeolite T membranes, the membrane synthesis precursor is mostly a milk-like aluminosilicate gel with a molar ratio of H_2O/SiO_2 of 14–16 [4–11] and the synthesis time is as long as 30 h. Thus, the formed membrane is as thick as 10–20 μm, which will decrease its permeate flux [4–11]. Recently, we reported the preparation of zeolite T membranes using a clear aluminosilicate solution with the molar ratio of H_2O/SiO_2 of 25 [12,13] or using a two-stage temperature-varying synthesis method with

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microsized seeds [15]. We also reported the fast synthesis of zeolite T membranes within only 6 h in a fluoride medium [14], showing high selectivity for water/organics mixtures by PV. However, to our best knowledge, there are few reports on the details of the synthesis of zeolite T membranes from clear solutions. The effects of synthesis parameters on membrane growth and PV properties are not clearly understood. Moreover, the poor reproducibility of zeolite membranes arouses attention because it will raise the preparation cost and influence the large-scale application of zeolite membranes.

In the present study, a well-intergrown zeolite T membrane with enhanced permeation properties was rapidly hydrothermally synthesized from clear solutions. The influence of synthesis parameters on membrane growth and permeation performance was investigated systematically. The as-synthesized membranes displayed a high PV performance for water/organics mixtures separation and high reproducibility.

2. Experimental

2.1. Membrane synthesis

Zeolite T membranes were synthesized by the seeded secondary growth method on 100 mm long porous mullite tubes (Nikkato Corp.). The tubes had an outer diameter of 12 mm, a wall thickness of 1.5 mm, an average pore size of 1.3 μm, and a porosity of ~43%. The tubes were polished with SiC sandpaper, washed in deionized water in an ultrasonic bath, and then dried in an oven at 373 K for 6 h. Before the hydrothermal synthesis, the support tubes were rub-coated with a water slurry of zeolite T powder, which was described elsewhere [13–15]. Microsized zeolite seeds were prepared from aluminosilicate gel with a molar composition of $1SiO_2$:$0.055Al_2O_3$:$0.24Na_2O$:$0.08K_2O$:$12H_2O$ [15]. The gel was mixed with precipitated silica (98 wt% SiO_2, Degussa VN3), $Al(OH)_3$ (Wako Pure Chemical), NaOH (Aldrich), KOH (Aldrich), and distilled water, followed by aging at room temperature for 12 h and crystallization at 373 K for 96 h. The products were recovered by centrifugation, washed with hot water, and dried at 393 K overnight. The seeds had a rod-like shape with an average size of 2.5 μm × 0.5 μm [15].

The clear synthesis solutions were prepared by mixing colloidal silica (TM-40, 40 wt% SiO_2, Aldrich), $Al(OH)_3$, NaOH, KOH, and distilled water, followed by vigorous stirring at room temperature for 1 h. The molar composition of the resulting solutions was $1SiO_2$:$(0.0005–0.020)Al_2O_3$:$(0.29–0.44)(Na_2O+K_2O)$:$(20–200)H_2O$ (with $n(Na)/n(K) = 3$). Then the seeded tube was vertically placed in a stainless steel autoclave filled with synthesis solution and the crystallization process was carried out at synthesis temperatures of 373 to 448 K for a given time. After crystallization, the membrane sample was taken out, washed carefully with hot deionized water, and dried.

2.2. Pervaporation measurements

Pervaporation tests were essentially the same as those described in our previous publications [12–15]. The inside of the membrane tube was evacuated by a vacuum pump. The permeate vapor was collected by a cold trap cooled with liquid nitrogen. The downstream pressure was kept below 20 Pa. The compositions of feed and permeate were analyzed by a gas chromatograph (GC, GC-14C, Shimadzu) equipped with a 3 m column packed with Polarpack Q poly(ethylene glycol)-1000. The permeation flux was calculated by weighing the condensed permeate. Based on the experimental data, the PV performance of the membrane can be characterized in terms of permeation flux (J, kg/(m²·h)) and separation factor (α) as shown below:

$$J = m/At$$

$$\alpha_{w/o} = (y_w/y_o)/(x_w/x_o)$$

where m is the mass of permeate collected over a period time (t), A is the effective membrane area for permeation, and x_w, x_o, y_w, and y_o denote the mass fractions of water and organics at the feed and permeate sides, respectively. Unless otherwise noted, the pervaporation tests were carried out with 10 wt% water-90 wt% *i*-propanol mixtures at 348 K.

2.3. Characterization

The crystal structure of zeolite seeds and as-synthesized membranes were characterized by X-ray diffraction (XRD, Ultima IV, Rigaku) with Cu K_α radiation at 40 kV and 120 mA. The morphology and thickness of the zeolite membranes were examined using a scanning electron microscopy (SEM, VEGA3 SBU, Tescan).

3. Results and discussion

3.1. Effect of SiO_2/Al_2O_3 ratio

Figure 1 shows the PV performance of zeolite T membranes prepared in the synthesis solutions of $1SiO_2$:$(0.0005–0.020)Al_2O_3$:$0.35(Na_2O+K_2O)$:$30H_2O$ at 423 K for 18 h. It can be seen that the SiO_2/Al_2O_3 ratio, which ranged from 50 to 2000, strongly influenced the PV performance. The permeation flux greatly increased with increasing SiO_2/Al_2O_3 ratio when the ratio was less than 66.7, whereas the flux rapidly decreased when the ratio was over 66.7. Moreover, the separation factor showed a similar trend. When the SiO_2/Al_2O_3 ratio was 66.7

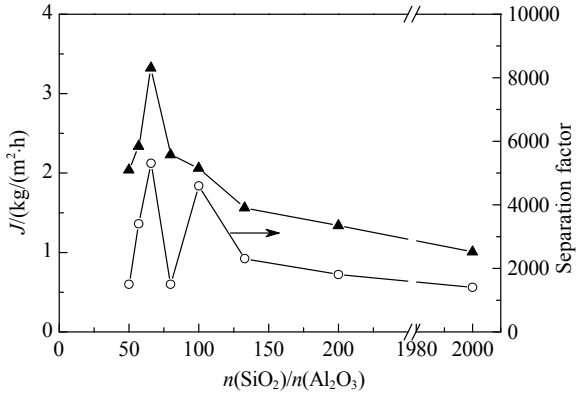

Fig. 1. Effect of SiO_2/Al_2O_3 ratio on the PV performance of the as-synthesized membranes.