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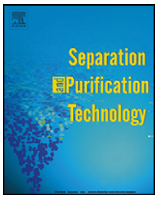

Preparation and gas permeation of nano-sized zeolite NaA-filled carbon membranes

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ABSTRACT

Nano-sized zeolite NaA crystal-filled carbon membranes were prepared on the inner surface of porous tubular alumina supports by dip-coating method, using the precursor solutions prepared by dispersing different amounts of nano-sized zeolite NaA particles in the alcohol solutions of phenolic resin. Single gas permeation measurements were carried out to examine the gas separation properties of the membranes. It was found that the zeolite NaA-filled carbon membranes showed higher ideal selectivities but lower single gas permeances than the pure carbon membranes when all the membranes were prepared with two cycles of preparation processes. When the nano-sized zeolite NaA content was 2 wt.% in the precursor solution, the resulting carbon membrane exhibited highest O_2/N_2 permselectivity of 14.6 and CO_2/N_2 permselectivity of 159. Higher or lower zeolite NaA content than 2 wt.% in the precursor solutions resulted in lower ideal selectivities of the gas pairs of the corresponding membranes. The change of the gas permeance with temperature of the zeolite NaA-filled carbon membrane was similar to that of the pure carbon membranes, indicating the similar gas permeation mechanism through the two kinds of membranes.

1. Introduction

Gas separation is a very important industrial process. Utilization of membranes for gas separation has some advantages over other kinds of gas separation processes, such as adsorption and cryogenic distillation, in terms of energy saving and simple operation. Inorganic microporous membranes have showed advantages in the separation of gases over polymeric gas separation membranes under such conditions as high temperatures. There are mainly two kinds of inorganic microporous gas separation membranes: zeolite or zeolite-like membranes, such as zeolite A [1–3], zeolite Y [4], ZSM-5 [5], ETS-10 [6], SAPO-34 membranes [7,8], etc., and carbon membranes [9,10]. Some other inorganic microporous membranes, such as silica membranes, prepared by sol–gel method [11], or chemical vapor deposition method [12], are also explored and used for gas separations.

Carbon membranes have showed good gas separation properties since the first successful preparation of a carbon membrane by Koresh and Sofer [13]. They are usually prepared by pyrolyzing polymer membranes or polymer precursors pre-coated on the supports. In order to improve or adjust the gas separation properties of the carbon membranes, several techniques are utilized during the preparation procedures. One is to oxidize the carbonized membranes or the polymeric precursor films before carbonization [14]. In this case, adsorption-selective carbon membranes can be prepared and can be used for the separation of gas mixtures containing adsorbable and non-adsorbable components. Another is to incorporate inorganic particles or fillers, such as nano-sized silver and nickel, into the carbon matrix [15,16]. Enhancements of the selectivities are observed for these modified carbon membranes compared to the pure carbon membranes. Since there are many kinds of nano-materials, there should be many possibilities to prepare nano-particles filled or incorporated carbon membranes, which will exhibit enhanced gas separation properties. However, research in this area is still rare.

Incorporation of inorganic particles or fillers into polymeric materials has been examined for many applications, and in particular, in the past decade, polymeric mixed matrix membranes using zeolites or carbon molecular sieves have been actively pursued for pervaporation applications [17]. There has however been limited research focused specifically on using mixed matrix (inorganic fillers and organic membranes) membranes in gas separations [17]. Consequently, reports on the preparation of inorganic particles-filled inorganic membranes are quite few. It

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is expected that inorganic particles-filled inorganic membranes exhibit enhanced gas separation properties, just as what inorganic particles-filled polymeric membranes do. On the other hand, inorganic particles-filled inorganic membranes apparently have advantage over inorganic particles-filled polymeric membranes, with the former usually showing higher gas permeances and being able to be used at higher temperatures. Shiflett and Foley [18], added zeolite (SSZ-13) or titanium dioxide to the polymer precursor in synthesizing the coatings for carbon membranes, which increased the gas fluxes while maintaining excellent ideal gas selectivities of the carbon membranes. No further research report has been seen since then. In most reports, micron-sized inorganic particles were used as the fillers. Utilization of nano-sized inorganic particles would have some advantages over the micron-sized particles because of the much smaller sizes and bigger outer surface areas of the nano-particles.

Zeolites have been actively utilized as the fillers in polymeric membranes in the past decade. The resulting mixed matrix membranes are usually pursued for pervaporation application, and research on zeolite-filled inorganic membranes for gas separation is few [18]. In this paper, we reported the preparation of nano-sized zeolite NaA particles filled carbon membranes. Zeolite NaA was chosen because of its quite small nominal pore size of 4 Å. The incorporation of nano-sized zeolite NaA into the carbon matrix would create a synergic effect for the composite carbon membranes, resulting in enhanced gas separation properties of the membranes.

2. Experimental

2.1. Materials

Nano-sized zeolite NaA powders were prepared by using in situ thermoreversible polymer hydrogels [19]. Briefly, a synthesis solution was prepared by adding methylcellulose (MC) powder into a zeolite synthesis gel with a molar composition of $5.85Na_2O:2.7SiO_2:1.00Al_2O_3:182H_2O$ to form the synthesis system with a weight composition of $3.56Na_2O:1.59SiO_2:1.00Al_2O_3:32.12H_2O:3.48MC$. Then, zeolite crystallization was carried out at 80 °C for 3 h. Finally, zeolite nanocrystals were recovered from the mother liquor by repeated cycles of centrifugation, decanting, and ultrasonic redispersion in pure water until MC was completely washed away (no bubbles were observed). Before use, the crystals were dried at 100 °C overnight. Phenolic resin (Tamanol 758, gift from Arakawa Chemical (USA) Inc.) was used as the carbon source. The home-made membrane support had a multilayered structure consisting of a coarse α-Al_2O_3 tube (12 mm o.d., 7 mm i.d., 50 mm length, and 5 μm mean pore diameter) coated with finer layers of γ-Al_2O_3 layer (0.2 μm mean pore diameter). Two ends of the supports were glazed, and then they were modified with the boehmite sol for three cycles following the method reported by Uhlhorn et al. [20].

2.2. Membrane preparation

The nano-sized zeolite NaA particles filled carbon membranes were prepared by the conventional dip-coating method [21]. The coating solutions were prepared by first completely dissolving phenolic resin in ethanol, followed by adding ground nano-sized zeolite powers slowly into the above phenolic resin solution with vigorous stirring and then ultrasonic vibration for 10 min. Right after the preparation of the coating solution, the support, wrapped with a layer of Teflon tape on the outside surface, was dipped into the solution for 3 min. Then it was taken out at a speed of about 1 mm/s, and was set vertically and upside down at room temperature for 24 h, followed by vacuum drying at room temperature for 6 h. Afterwards, it was carbonized at a heating rate of 1 °C/min in N_2 to 600 °C with a dwell time of 2 h. The coating and carbonization cycles were repeated for one more time under the same condition to obtain the final membranes.

2.3. Characterization

The purity of the nano-sized zeolite NaA was determined by X-ray diffraction (XRD, Bruker D8-Advance). Its particle size and particle size distributaries were measured by laser-scattering analyzer (LSA, Mastersize 2000, Marlvin). Nano-sized zeolite particles and nano-sized zeolite NaA-filled carbon membranes were examined with scanning electron microscope (SEM, LEO-1530VP, Oxford). Element analysis in the cross-section of the carbon membrane was carried out with energy dispersive X-ray analysis (EDX, Sigma).

2.4. Permeation measurements

Single gas permeation measurements were carried out using H_2, CO_2, O_2, and N_2 by a dead-end method. The membrane was sealed with graphite ferrules in a stainless-steel tube-shell assemble with one dead end and the other one connected to a gas line. The whole system was vacuumed for 20 min before a gas was introduced. The flux through the membrane was measured using a bubble flow meter.

3. Results and discussions

3.1. Characterization of the nano-sized zeolite NaA particles and the membranes

Fig. 1 shows the XRD pattern of the nano-sized zeolite NaA, indicating a pure zeolite A phase. It was apparent that the diffraction peaks were broadening, referring small crystal size of the sample. Fig. 2 shows the particle size distribution of the zeolite sample measured by LSA. It could be seen that most of the zeolite crystals were in the range of 50–120 nm in size. SEM image of the particles (Fig. 3) also shows uniform particle morphology and small particle size. The difference between the LSA results and SEM results is probably due to the surface salvation effect in LSA [22].

Fig. 4 shows the SEM image and EDX analysis spectrum of the cross-section of a nano-sized zeolite NaA-filled carbon membrane prepared with 2 wt.% zeolite, 40% phenolic resin alcohol solution,

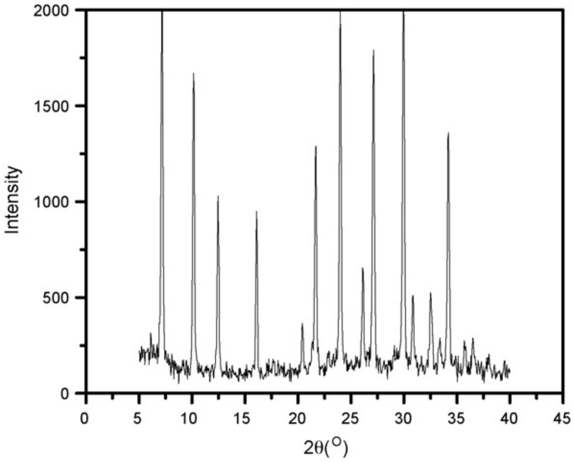

Fig. 1. XRD patterns of the nano-sized zeolite NaA crystals.