Gas permeation properties through Al-doped organosilica membranes with controlled network size

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ABSTRACT

The sol–gel method was applied to the fabrication of Al-doped bis (triethoxysilyl) methane (BTESM)-derived membranes. The single-gas permeation properties for Al-doped BTESM-derived membranes were examined to evaluate the effect of aluminum concentration on amorphous silica network sizes. Each permeance was decreased with an increase in the Al concentration, and the H_2/CH_4 and H_2/C_3H_8 permeance ratios increased with an increase in Al concentration. For example, an Al-doped BTESM (Si/Al=8/2) membrane fabricated at 200 °C showed a H_2 permeance of 4.4×10^{-7} mol m^{-2} s^{-1} Pa^{-1}, which was approximately 1/10th that of a BTESM membrane fabricated at 200 °C. The H_2/CH_4 and H_2/C_3H_8 permeance ratios were 60 and 2700 with Al doping, but 30 and 1000 without Al-doping, respectively. The activation energy of He, H_2, N_2, and CH_4 permeation was increased with an increase in the Al concentration, indicating that the pore size of BTESM-derived networks was decreased with an increase in Al concentration. The decrease in BTESM-derived network sizes that resulted from an increase in the Al concentration can be ascribed to the absolute amount of Al incorporated into BTESM-derived networks and/or coordinated with Si-OH groups, as suggested by ^{27}Al MAS NMR. High C_3H_6/C_3H_8 permeance ratios of approximately 40 for Al-doped BTESM (Si/Al=9/1) membranes fabricated at 200 °C were achieved through the precise control of the silica network size via a spacer method using Si–C–Si units as well as the incorporation of Al in BTESM-derived networks.

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1. Introduction

The separation of olefin and paraffin is one of the most important processes in the petrochemical industry and is currently carried out by cryogenic distillation with an exhorbitant amount of energy consumption. The membrane-based separation of olefin from paraffin is considered quite attractive as a simple and energy-conserving separation method and offers many advantages, particularly gas separation with no phase change. Accordingly, many types of membranes have been developed for the separation of olefin from paraffin: polymer-electrolyte facilitated transport [1,2], polymer [3], carbon-molecular sieve [4–7], zeolite [8–12], and amorphous silica [13–15].

Recently, ZIF-8 membranes (ZIF-8, Zn(MeIM)$_2$, MeIM: 2-methyli-midazole), which possess six-ring β cages with pore sizes of approximately 0.4 nm, have been successfully synthesized using a hydrothermal seeded growth method and have shown excellent separation performance for propylene/propane binary mixtures

(C_3H_6 permeance: 2.0–3.0×10^{-8} mol m^{-2} s^{-1} Pa^{-1}, C_3H_6/C_3H_8 separation factor: ~45) [10]. These membranes showed much better separation performance by comparison with carbon membranes [4–7]. Hara et al. [11] reported that the diffusion-separation factor through ZIF-8 membranes prepared by counter-diffusion methods increased with decreasing temperature, reaching a maximum of 23, while the solubility-separation factor (=2.7) was independent of temperature, suggesting that high C_3H_6/C_3H_8 separation performance through ZIF-8 membranes could be ascribed mainly to being governed by diffusive separation. Organosilica membranes prepared by the "spacer" technique, which utilizes an organic functional group between 2 Si atoms as a "spacer" to control the pore size of amorphous silica networks, also showed high C_3H_6/C_3H_8 separation performance [14,15]. Bis (triethoxysilyl) methane (BTESM)-derived silica (Si–C–Si unit) membranes showed C_3H_6 permeance (0.28–6.3×10^{-7} mol m^{-2} s^{-1} Pa^{-1}) with a C_3H_6/C_3H_8 permeance ratio (6.9–33) at 50 °C [14,15] that was approximately the same as those at 22 °C for ZIF-8 membranes [10]. High C_3H_6 separation performance can be achieved by the control of silica network size via a "spacer" method using a Si–C–Si unit.

Since the molecular size of C_3H_6 is similar to that of C_3H_8, the precise control of the average pore size of a membrane is quite

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important in order to achieve high C_3H_6/C_3H_8 selectivity by the molecular sieving mechanism. In addition, the enhancement of adsorption properties, particularly for C_3H_6 molecules with a C=C bond (π-bond), is also important in order to achieve high C_3H_6/C_3H_8 selectivity by blocking the permeation for C_3H_8 molecules by preferentially adsorbed C_3H_6 molecules under binary-component separation. Several studies have reported the enhancement of olefin adsorption properties by using metal ions such as Ag^+ and Cu^+, which creates π-complexation interactions between the double bond of olefin and transition metal cations [16–18]. Stoitsas et al. [18] reported the equilibrium adsorption isotherms of C_3H_6 and C_3H_8 over microporous SiO_2 and Ag^+/SiO_2 gels. The adsorption selectivity for C_3H_6 was dramatically enhanced by using Ag^+ and showed a value of 150 at 1 bar, which was approximately 50 times greater than that for unmodified SiO_2. Those researchers concluded that the enhancement of C_3H_6 selectivity could be ascribed to the presence of Ag^+ ions acting in a two-fold manner, i.e., by partially blocking the microporous system in a way that hindered the diffusion and/or sorption of C_3H_8 molecules and simultaneously introduced a C_3H_6 selective adsorption site [18].

In our previous study, aluminum was selected as a doping material with the expectation of promoting an increase in adsorptive sites only for C_3H_6 molecules, which could be facilitated by the interaction between the π-bond of C_3H_6 molecules and the electric charge balance of Al ions, as well as by an enhancement of the molecular sieving effect through the precise control of the BTESM-derived (Si–C–Si unit) network size [19]. The C_3H_6/C_3H_8 permeation properties through Al-doped BTESM-derived membranes strongly depended on the fabrication temperatures. When an Al-doped BTESM-derived membrane was fabricated at 350 °C, it demonstrated a C_3H_6/C_3H_8 permeance ratio of 1.4, which was much smaller than that for BTESM membranes. The decreased C_3H_6/C_3H_8 permeance ratio through an Al-doped BTESM membrane was ascribed to the formation of disordered networks, which was caused by the formation of a Q^4 unit in the BTESM-derived networks. On the other hand, when an Al-doped BTESM-derived membrane was fabricated at 200 °C, a high C_3H_6/C_3H_8 permeance ratio of 25–35 at 200 °C was obtained due to the precise control of the silica network size via the spacer method using a Si–C–Si unit without disordered networks, as well as via the incorporation of Al into the BTESM-derived networks. However, additional study is needed to evaluate the effect of Al concentration on C_3H_6/C_3H_8 permeation properties and amorphous network sizes. In the present study, Al-doped BTESM-derived membranes were fabricated at 200 °C with different aluminum concentrations (Si/Al molar ratio: 9.5/0.5, 9/1, 8/2), and single gas permeation properties were evaluated for temperatures that ranged from 50 to 200 °C. The effect of doped aluminum concentrations on Al-doped BTESM networks were also evaluated based on ^{27}Al MAS NMR and N_2 adsorption properties.

2. Experimental

2.1. Preparation of the Al-doped BTESM sol and membrane fabrication

Al-doped BTESM sol was prepared by the hydrolysis and polymerization reaction of BTESM in ethanol with water, $Al(NO_3)_3 \cdot 9H_2O$ and HNO_3 [19]. A specified amount of BTESM, $Al(NO_3)_3 \cdot 9H_2O$ and water in ethanol under HNO_3 as a catalyst was stirred at 25 °C for 12 h. The composition of the solution was $BTESM/EtOH/H_2O/HNO_3 = 1/28/200/0.1$ in a molar ratio, and the weight % of BTESM was kept at 5.0 wt%. The Si/Al molar ratios were controlled at 9.5/0.5, 9/1 and 8/2.

Porous α-alumina tubes (porosity: 50%, average pore size: 1 μm, outside diameter: 10 mm) were used as supports for the Al-doped BTESM-derived membranes. Two types of α-alumina particles (average particle diameter: 0.2, 1.9 μm) were coated onto the outer surface of a porous support using a silica–zirconia colloidal sol as the binder, and the support was fired at 550–600 °C for 30 min to smooth the surface. These procedures were repeated several times to cover any large pores that might have resulted in pinholes in the final membrane. SiO_2–ZrO_2 (Si/Zr = 1/1) sol, diluted to about 0.5 wt%, was then coated onto the substrate to form an intermediate layer with pore sizes of 2–3 nm [14,15]. After coating, the membrane was fired at 550–600 °C for about 30 min. Finally, the Al-doped BTESM-derived layer was fabricated by coating with Al-doped BTESM sol (Si/Al = 9.5/0.5, 9/1, 8/2), followed by drying and calcination at 200 °C for 30 min under an air atmosphere.

2.2. Characterization of the Al-doped BTESM gel

Al-doped BTESM-derived gel powder (Si/Al = 9.5/0.5, 9/1, 8/2) was prepared by drying at 40 °C under air, followed by calcination at 200 °C under an air atmosphere for 30 min, and grinding using a mortar. *In-situ* transmittance FT–IR spectra for BTESM-derived and Al-doped BTESM-derived films coated on the silicon wafer plate and calcined at 200 °C were recorded using a FT–IR spectrometer (FT/IR-4100, Jasco, Japan) at 200 °C under an air atmosphere (200 cm^3 min^{-1}) after being kept for 2 h to remove the adsorbed water molecules. The adsorption isotherms of C_3H_6 and C_3H_8 for Al-doped BTESM-derived powder fired at 200 °C under an air atmosphere were measured at 20 °C under pressures that ranged from 0 to 100 kPa (BELMAX, BEL JAPAN INC.). Measurements of N_2 adsorption (at 77 K) for the powder samples were also carried out using BELMAX.

The ^{27}Al magic angle spinning (MAS) NMR spectra were recorded at 104.2 MHz on a Varian 600 PS solid NMR spectrometer, using a 3.2 mm-diameter zirconia rotor. The rotor was spun at 15 kHz for ^{27}Al MAS NMR. The spectra were acquired using 2.3 μs pulses, a 1 s recycle delay, and 1000 scans for ^{27}Al MAS NMR. $Al(NO_3)_3 \cdot 9H_2O$ was used as a chemical shift reference for ^{27}Al. Prior to the ^{27}Al MAS NMR measurements, the samples were moisture equilibrated over a saturated solution of NH_4Cl for 24 h.

2.3. Single-gas permeation measurement

Fig. 1 shows a schematic diagram of the experimental apparatus for a single-gas permeation measurement. A single industrial-grade gas (He, H_2, CO_2, N_2, CH_4, C_3H_6, C_3H_8, SF_6) was fed on the outside (upstream) of a cylindrical membrane at 200 kPa, keeping the downstream at atmospheric pressure. The temperature of the permeation cell was kept at a given temperature of between 50 and 200 °C. The permeation rate was measured using a bubble film meter. The deviation in the permeation data was less than 5%.

3. Results and discussion

3.1. Gas permeation properties through Al-doped BTESM-derived membranes

Fig. 2 shows the SEM image of the cross-section of an Al-doped BTESM-derived membrane (Si/Al = 9/1). Although it is quite difficult to distinguish the organosilica layer from the SiO_2–ZrO_2 intermediate layer, a thin, continuous organosilica separation layer can be seen on the top and/or inside of the SiO_2–ZrO_2 intermediate layer. The thickness of the active separation layer was clearly less than 1 μm. It should be noted that both the thickness of the active