Electronic Supplementary Information

Pore size control of Al-doping into bis (triethoxysilyl) methane (BTESM)-derived membranes for improved gas permeation properties

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Experimental

Preparation of Al-doped BTESM-derived silica sol and membrane fabrication

Al-doped BTESM-derived 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. A specified amount of BTESM, $Al(NO_3)_3{\cdot}9H_2O$ and water in ethanol under HNO_3 as a catalyst were stirred at 25 ^oC 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 ratio was controlled at 9/1, 8.5/1.5, 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 silica membranes. Two types of α-alumina particles (average particle diameter: 0.2, 1.9 μm) were coated on the outer surface of a porous support using silica-zirconia colloidal sol as the binder, and the support was fired at 550-600 ^oC for 30 minutes to make the surface smooth. These procedures were repeated several times to cover large pores that might result in pinholes in the final membrane. SiO_2-ZrO_2 (Si/Zr=1/1) sol, diluted to about 0.5 wt%, was then coated on the substrate to form an intermediate layer. After coating, the membrane was fired at 550-600 ^oC for about 30 min. Finally, the Al-doped BTESM-derived silica layer was fabricated by coating with Al-doped BTESM sol (Si/Al=9/1, 8.5/1.5, 8/2), followed by drying and calcination at 200 and 350 ^oC for 30 min in an air atmosphere, respectively.

Figure S1 shows the SEM image of a cross-section of an Al-doped BTESM-derived silica membrane (Si/Al=9/1). Although it is quite difficult to distinguish the silica layer from the SiO_2-ZrO_2 intermediate layer, a thin, continuous silica 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 is clearly less than 1 μm.

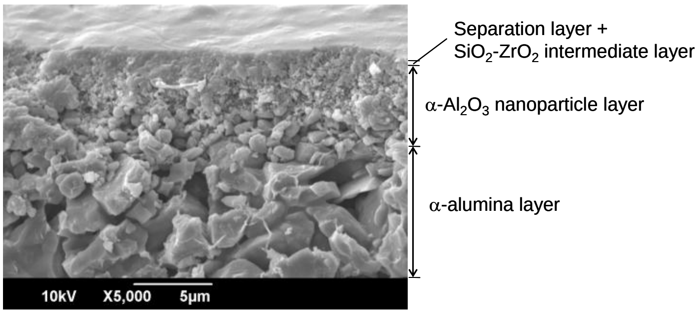

Figure S1 SEM image of a cross-section of an Al-doped BTESM-derived silica membrane.

Characterization of Al-doped BTESM-derived silica gel

Al-doped BTESM-derived gel powder (Si/Al=9/1) was prepared by drying at 40 ^{o}C in air, followed by calcination at 200-350 ^{o}C in an air atmosphere for 30 min, and ground using a mortar. The XRD measurements were performed by step-wise scanning (2θ step-size: 0.025 ^{o}, 15 ^{o} < 2θ < 80 ^{o}, RINT2000, RIGAKU Co. Japan).

The ^{27}Al magic angle spinning (MAS) NMR and ^{29}Si MAS NMR spectra were recorded at 104.2 MHz and 79.5 MHz, respectively, on a Varian 600PS solid NMR spectrometer, using a 3.2-mm-diameter zirconia rotor for ^{27}Al MAS NMR and a 6-mm-diameter zirconia rotor for ^{29}Si MAS NMR. The rotor was spun at 15 kHz for ^{27}Al MAS NMR and at 6 kHz for ^{29}Si MAS NMR. The spectra were acquired using 2.3 μs pulses, a 1 s recycle delay, and 1,000 scans for ^{27}Al MAS NMR, and 5 μs pulses, a 100 s recycle delay, and 1,000 scans for ^{29}Si MAS NMR. $Al(NO_3)_3 \cdot 9H_2O$ and $Si(CH_3)_4$ were used as chemical shift references for ^{27}Al and ^{29}Si MAS NMR, respectively. Prior to the ^{27}Al MAS NMR measurements, the samples were moisture equilibrated over a saturated solution of NH_4Cl for 24 h.

Single gas permeation measurement

Figure S2 shows a schematic diagram of the experimental apparatus for single gas permeation measurement. A single industrial-grade gas (He, H_2, CO_2, O_2, N_2, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, i-C_4H_{10}, 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 between 50 and 200 ^{o}C. The permeation rate was measured using a bubble film meter. The deviation in the permeation data was less than 5%.

Binary-component gas separation tests were performed at a given temperature between 50 and 200 ^{o}C with gas mixtures of C_3H_6 and C_3H_8, which were fed on the outside (upstream) of the cylindrical membrane module at 200 kPa, keeping the downstream pressure constant at atmospheric pressure. The upstream and downstream flow rates were measured by a bubble film meter, and the gas compositions were analyzed by gas chromatography using a TCD detector (column: Unibeads 1S 80/100, GL Science, Japan).

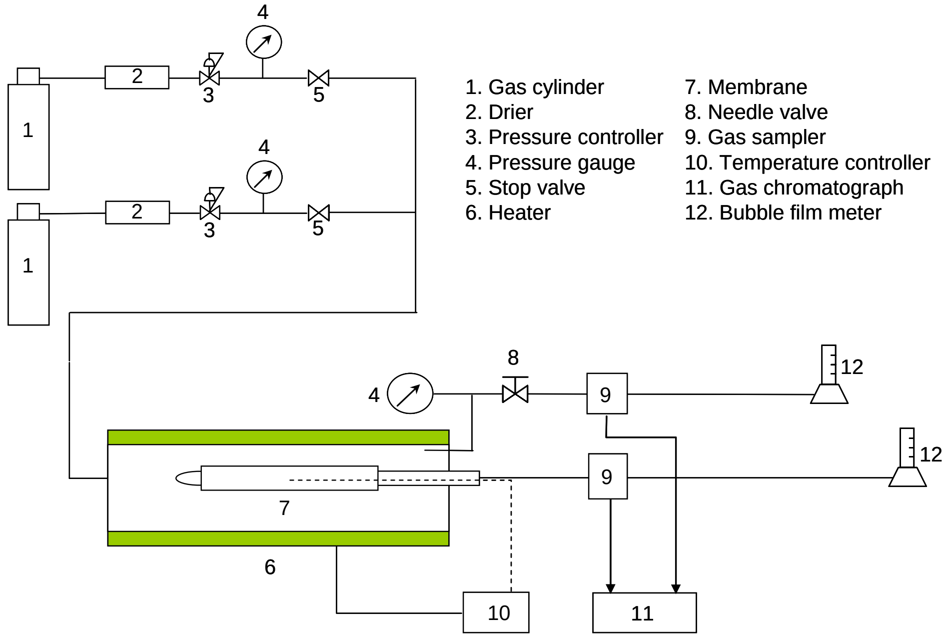

Figure S2 Schematic diagram of the experimental apparatus for single gas permeation measurement.

Average pore size estimated by dimensionless permeance based on He permeance

Figure S3 shows the dimensionless permeance based on He permeance at 200 °C for BTESM-derived and Al-doped BTESM-derived silica membranes (Si/Al=9/1, 8.5/1.5, 8/2) as a function of molecular size. The broken line shows the calculated dimensionless permeance under Knudsen mechanism based on He. An Al-BTESM-350 (Si/Al=8.5/1.5) membrane showed the sharpest cutoff between He and CO_2 (permeance ratio: 200), which was much higher than the value expected in the case of the Knudsen diffusion mechanism (He/CO_2 Knudsen selectivity: 3.32). The permeation cutoff of a BTESM-350 membrane appeared to roughly follow the Knudsen mechanism in the range of He (0.26 nm) to CO_2 (0.33 nm). An Al-BTESM-350 (Si/Al-9/1) membrane showed a much higher He to CH_4 and C_3H_8 permeance ratio in comparison with that for a BTESM-350. These results suggest that the estimated order of the average pore size is as follows: BTESM-350 > Al-BTESM-350 (Si/Al=9/1) > Al-BTESM-350 (Si/Al=8.5/1.5, 8/2).

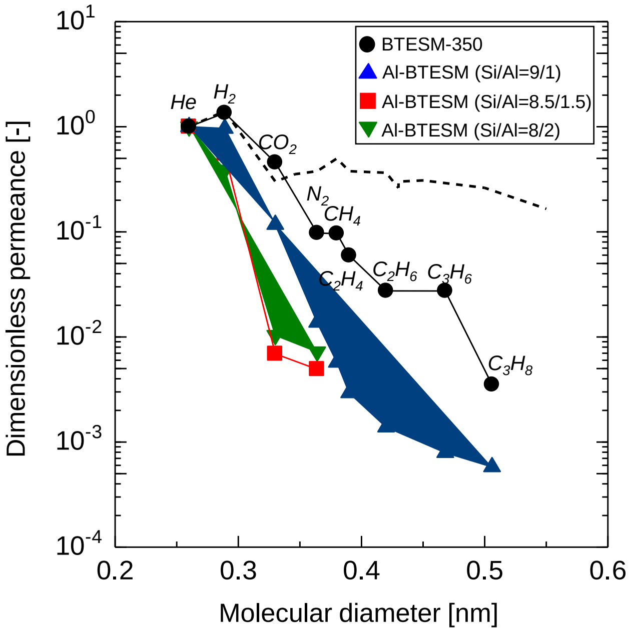

Figure S3 Dimensionless permeance based on He permeance at 200 °C for BTESM-derived and Al-doped BTESM-derived silica membranes (Si/Al=9/1, 8.5/1.5, 8/2) as a function of molecular size.

Temperature dependence of C_3H_6 and C_3H_8 permeances through Al-doped BTESM membranes (Al-BTESM-200 (Si/Al=9/1), Al-BTESM-350 (Si/Al=9/1))

Figure S4 compares temperature dependence of C_3H_6 and C_3H_8 permeances for Al-doped BTESM-derived (Si/Al=9/1) membranes calcined at 200 and 350 °C. The permeance of C_3H_6 for an Al-BTESM-200 (Si/Al=9/1) slightly increased with an increase in temperature, which is somewhat akin to an activated permeation mechanism. It should be noted that the permeation mechanism of adsorptive molecules such as C_3H_6 and C_3H_8 is governed by the balance between the kinetic diffusivity, depending on the ratio of molecular and pore size, as well as the concentration gradient by adsorption, depending on temperature and pressure. The permeation property of C_3H_6 molecules through an Al-BTESM-200 (Si/Al=9/1) tended to be dominated by molecular sieving rather than adsorption. The permeance of C_3H_8 for an Al-BTESM-200 (Si/Al=9/1) was independent of temperature. The permeance ratio of C_3H_6/C_3H_8 for an Al-BTESM-200 (Si/Al=9/1) slightly decreased with a decrease in temperature. The permeance of C_3H_6 and C_3H_8 slightly increased with decreasing temperature, indicating that the Knudsen mechanism is dominant for the permeation of these molecules.

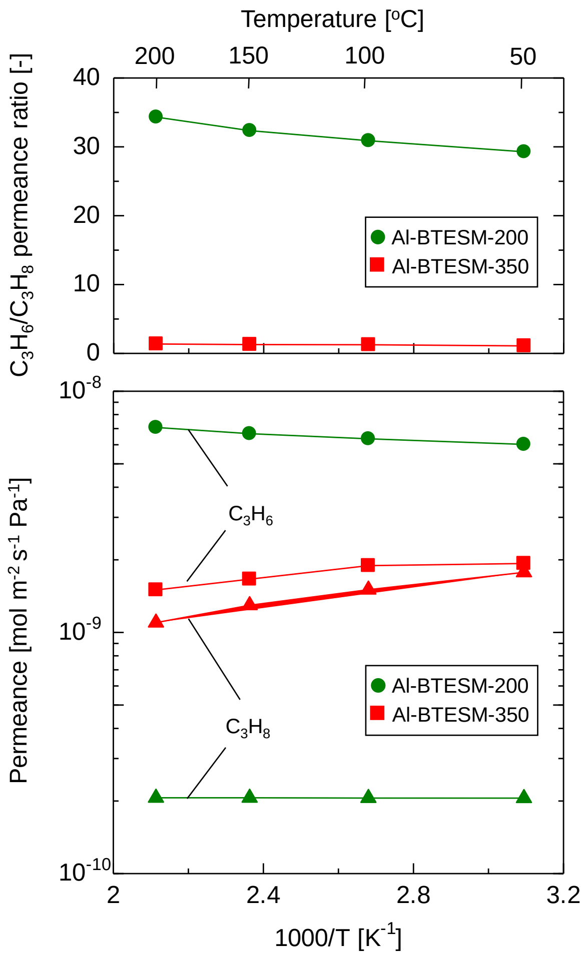

Figure S4 Temperature dependence of C_3H_6 and C_3H_8 permeances for Al-doped BTESM-derived membranes calcined at 200 and 350 ^oC.

Binary-component gas separation of C_3H_6 and C_3H_8 for an Al-doped BTESM membrane (Al-BTESM-200 (Si/Al=9/1))

Figure S5 shows the observed separation results of C_3H_6/C_3H_8 at 50 ^oC for Al-BTESM-200 (Si/Al=9/1). The predicted separation curves in this figure were obtained by the following equation at low cut [M. Kanezashi et al., *Sep. Sci. Technol.*, 2005, **40**, 225.].

$$Y_A = \frac{\beta - \sqrt{\beta^2 - 4\gamma(\alpha - 1)\alpha X_A}}{2\gamma(\alpha - 1)} \quad (1)$$

where Y_A is the mole fraction of gas A in permeates (downstream), X_A is the mole fraction of gas A in the feed (upstream), α is the permeance ratio, $\beta = (\alpha - 1)(X_A + \gamma) + 1$, P_u is the upstream total pressure, P_d is the downstream total pressure, and $\gamma = P_d/P_u$. In the present study, binary-component gas separation was conducted with a ratio of Pu/Pd=2 (Pu=200 kPa, Pd=100 kPa) at 200 ^oC. The broken curve is the calculated results with α obtained by single gas permeation, while the solid curve is fitted with a permeance ratio of 25. The C_3H_6/C_3H_8

permeance ratio obtained by binary component separation (α=25) was much higher than that obtained by single gas permeation (α=20), indicating that preferentially adsorbed C_3H_6 molecules block the permeation of C_3H_8 molecules.

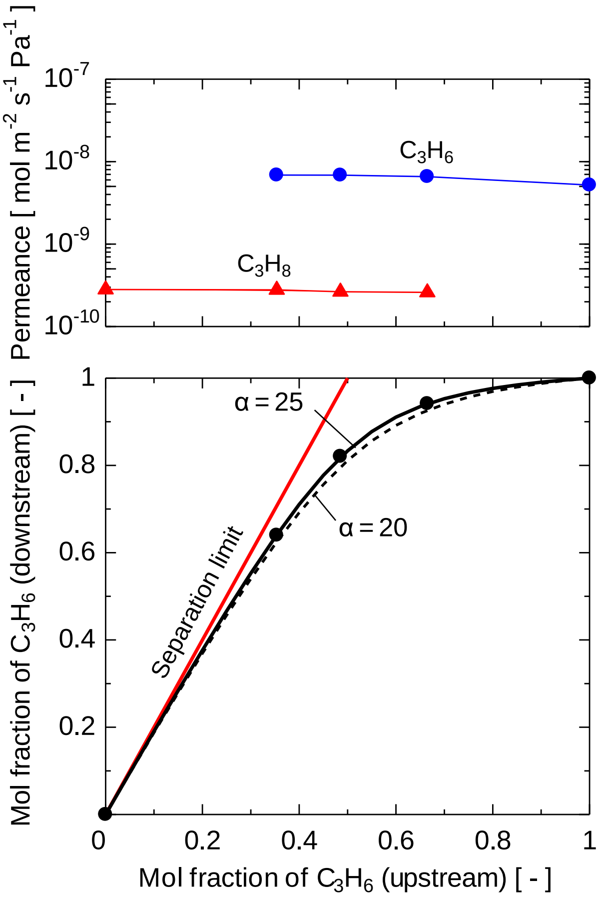

Figure S5 Separation results of C_3H_6/C_3H_8 mixtures at 50 °C for an Al-BTESM-200 (Si/Al=9/1).

XRD patterns of Al-doped BTESM-derived gels

Figure S6 shows the XRD patterns for Al-BTESM-350 (Si/Al=9.5/0.5, 9/1, 8.5/1.5) gel powders calcined at 350 °C in an air atmosphere. Al-BTESM-350 gel powders showed an amorphous structure, irrespective of Al content. Based on the XRD analysis of Al-BTESM-350 powders, the doped Al was incorporated in the silica matrix, which could be impregnated in the silica matrix as metal ions and covalently bound compounds such as Si-O-Al-. These results agree well with the ^{27}Al MAS NMR spectra, as shown in the manuscript (Fig. 4).

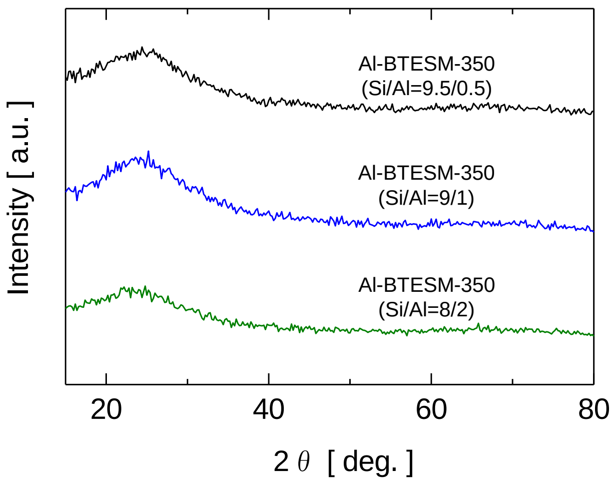

Figure S6 XRD patterns for Al-BTESM-350 (Si/Al=9.5/0.5, 9/1, 8.5/1.5) gel powders calcined at 350 ^{o}C in an air atmosphere.