Fluorine Doping of Microporous Organosilica Membranes for Pore Size Control and Enhanced Hydrophobic Properties

Masakoto Kanezashi,* Masaaki Murata, Hiroki Nagasawa,* and Toshinori Tsuru*

Department of Chemical Engineering, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

Supporting Information

ABSTRACT: Fluorine-doped organosilica membranes for gas and pervaporation (PV) separation were fabricated using a sol–gel method. NH₄F and bis(triethoxysilyl)methane (BTESM) were selected as the dopant and Si precursor, respectively, for the fabrication of fluorine-doped organosilica membranes. Doping with fluorine was evaluated for its effect on the physicochemical properties of organosilica (hydrophobicity/hydrophilicity and network size). Fluorine doping dramatically eliminated the formation of Si–OH groups in the sol, so that the condensation of Si–OH groups during the calcination process was suppressed. It is possible that fluorine doping enlarged the network pore sizes in organosilica, because the F-BTESM (F/Si = 1/9) membrane showed superior He and H₂ permeance with a low H₂/N₂ permeance ratio that corresponded to the network pore size by comparison with an undoped BTESM membrane. The F-BTESM (F/Si = 1/9) membranes showed a high level of C₃H₆ permeance (≈3.0 × 10⁻⁷ mol m⁻² s⁻¹ Pa⁻¹) with a high C₃H₆/SF₆ permeance ratio (~250), which suggests that the network size of F-BTESM is suitable for the separation of large molecules such as hydrocarbon gases (C₃/C₄, C₄ isomer, etc.). Organosilica membranes both with and without fluorine doping showed stable PV performance because of the fact that H₂O permeance and each permeance ratio under different separation systems was approximately constant over 10 h at 70 °C. Fluorine doping enhanced the hydrophobic nature of the organosilica, which was confirmed by the H₂O adsorption and PV properties.

1. INTRODUCTION

Amorphous SiO₂ membranes with pore sizes in the sub-nanometer range have great potential for application to gas/liquid separation.¹⁻³ Membrane performance (selectivity, permeability) depends on the thickness and pore size of the separation layer, so that a thin microporous silica layer is coated onto an intermediate layer (γ-alumina,¹³ SiO₂–ZrO₂) to form a porous substrate, which makes it possible to form a layer-by-layer structure to decrease the permeation resistance. The utilization of silsesquioxane (RSiO₁.₅) categorized as either a pendant-type⁴⁻⁵ or a bridged-type⁶⁻¹⁴ Si precursor makes it possible to control the pore size of an amorphous structure as well as the hydrophobic/hydrophilic properties, respectively, because of the presence of nonhydrolyzable organic groups. The network structure of bridged-type organosilica utilizing bis(triethoxysilyl)methane (BTESM) and bis(triethoxysilyl)ethane (BTESE) via a sol–gel method is suitable for H₂/organic compounds⁸¹¹ and C₃H₆/C₃H₈¹⁰ separation, respectively, because the spacer (Si–CH₂–Si, Si–C₃H₆–Si unit) can work as a minimum unit in networks for the construction of a loose network structure.

The effect that a linking unit with a carbon number larger than 3 (Si–C₃H₆–Si) exerts on network pore size and on a microporous structure was also evaluated by fabricating organosilica membranes such as [bis(triethoxysilyl)propyl (BTESP), bis(triethoxysilyl)hexane (BTMSH), bis(triethoxysilyl)benzene, and bis(triethoxysilyl)octane (BTESO)].¹⁴ The network size determined by gas permeation properties became larger as the carbon number increased between 2 Si atoms, and H₂ selectivity was decreased as the carbon number between 2 Si atoms increased, but despite having larger network pore sizes, the BTESP (Si–C₃H₆–Si), BTMSH (Si–C₆H₁₂–Si), and BTESO (Si–C₈H₁₆–Si) membranes showed smaller values for gas permeance compared with either the BTESM or the BTESE membranes. The increased flexibility of the linking units in the structures of Si–C₃H₆–Si, Si–C₆H₁₂–Si, and Si–C₈H₁₆–Si membranes tended to collapse the micropores and decrease the porosity, which

Received: June 18, 2018
Accepted: July 24, 2018
Published: August 2, 2018
was confirmed by the measurement of N₂ adsorption properties. This tendency suggests that increased flexibility might not be appropriate for the formation of highly permeable membranes.

The incorporation of Si–F bonds in the SiO₂ structure via the addition of NH₄F and/or the utilization of triethoxyfluorosilane was an innovative strategy to control the physicochemical properties dictating the amorphous nature of SiO₂, which includes hydrophilicity/hydrophobicity and network pore size. Hydrophilic surface modification of porous media [mesoporous silica (MCM-41), zeolite] was successfully achieved by replacing the Si–OH groups with Si–F groups. The incorporation of Si–F bonds affected the Si–O–Si bond angle, and this change in the SiO₂ structure made it possible to form a loose and uniform structure rather than that of SiO₂. Highly permeable gas separation membranes such as CO₂/CH₄ (CO₂ permeance: 4.1 × 10⁻¹ⁱ m² s⁻¹ Pa⁻¹, CO₂/CH₄ permeance ratio: 300 at 35 °C) and C₃H₆/C₃H₈ (C₃H₆ permeance: 2.2 × 10⁻¹ⁱ m² s⁻¹ Pa⁻¹, C₃H₆/C₃H₈ permeance ratio: 42 at 35 °C) were tailored via a fluorine-induced SiO₂ matrix. The pore size distribution obtained by single-gas permeation showed that densification of the network structure for a fluorine-induced SiO₂ matrix was suppressed even under high temperatures and/or a hydrothermal atmosphere.

In the present study, NH₄F and BTESM were selected as the dopant and Si precursor, respectively, to fabricate fluorine-doped BTESM membranes that could then be used to evaluate the effect that fluorine doping exerts on the organosilica network size as well as on the gas permeation and pervaporation (PV) properties. The fluorine doping of a network structure was characterized via X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FT-IR) spectra, and N₂ adsorption properties. The hydrophobicity/hydrophilicity of organosilica was evaluated via H₂O adsorption.

2. RESULTS AND DISCUSSION

2.1. Effect of Fluorine Doping on the Physicochemical Properties of Organosilica. Figure 1 shows the FT-IR spectra for BTESM (a) and F-BTESM (F/Si = 1/9) (b) before and after calcination at 350 °C. The peak at around 1050 cm⁻¹ can be ascribed to the stretching of the smaller-angle Si–O–Si bonds in a network structure. The peak at 960–980 cm⁻¹ can be ascribed to the stretching of Si–OH bonds. Both asymmetric and symmetric C–H stretching vibrations of –CH₃ and –CH₂ fragments were detected at 2932 and 1350 cm⁻¹, respectively, irrespective of fluorine doping and with/without calcination. This indicated that organosilica networks with linking units (Si–CH₂–Si) were formed by the hydrolysis/condensation of the ethoxy and silanol groups, respectively. Interestingly, the F-BTESM (F/Si = 1/9) film showed fewer chemisorbed H₂O molecules (3400 cm⁻¹) compared with the BTESM film.

The peak area ratios for Si–OH (960–980 cm⁻¹)/Si–O–Si (1050–1100 cm⁻¹) in both samples before/after calcination at 350 °C are summarized in Table 1 to demonstrate the effect of fluorine doping on Si–OH groups. The BTESM film showed a higher value for the Si–OH/Si–O–Si peak area ratio compared with that of the F-BTESM film (F/Si = 1/9), but the peak area ratio was largely decreased after calcination. On the other hand, the F-BTESM (F/Si = 1/9) film showed a lower value for the Si–OH/Si–O–Si peak area ratio, and only a slight decrease was confirmed after calcination at 350 °C. Thus, fluorine doping eliminated the formation of Si–OH groups in the sol (before calcination), and the condensation of Si–OH groups was suppressed during the calcination process.

Table 1. Peak Area Ratio of Si–OH (960–980 cm⁻¹)/Si–O–Si (1050–1100 cm⁻¹) for BTESM and F-BTESM (F/Si = 1/9) Films before/after Calcination at 350 °C under an Air Atmosphere

|                     | before calcination | after calcination |
|---------------------|--------------------|-------------------|
| BTESM               | 0.24               | 0.06              |
| F-BTESM (F/Si = 1/9)| 0.06               | 0.03              |

Figure 2 shows the XPS spectra in the range of 0–1200 eV (a) and from 680 to 695 eV (b) for F-BTESM (F/Si = 1/9) powders calcined at 350 °C. The F/Si molar ratio was calculated from each peak area ratio: Si 2p at 104.6 eV; F 1s at 688 eV, and C–F at 685–687.5 eV. When NH₄F was doped into an amorphous SiO₂ structure derived from TEOS, the doped F was present as Si–F bonds, which could be detected at 688 eV. On the other hand, when NH₄F was doped into the organosilica structure derived from...
BTESM (Si−C−Si unit), only a slight peak at 688 eV was detected, and the largest peak was detected in the range of 685−687.5 eV, which can be ascribed to semi-ionic and covalent C−F bonds. F-BTESM (F/Si = 1/9) calcined at 350 °C showed approximately the same fluorine concentration as the fluorine-doped concentration (10 mol %) in the sol, which confirmed no direct decomposition of NH4F at 145−225 °C.29

Figure 3a shows the N2 adsorption isotherms at 77 K (0 < P/P0 < 0.1) for BTESM and F-BTESM (F/Si = 1/9) powders calcined at 350 °C under an air atmosphere. Both samples showed a trend whereby the adsorbed amount of N2 increased with increase in the relative pressure, indicating microporous properties. However, the slope of F-BTESM (F/Si = 1/9) was higher than that of BTESM. Fluorine doping effectively increased the Brunauer−Emmett−Teller (BET) surface area and pore volume, as summarized in Table 2.

Table 2. Pore Volume (MP) and BET Surface Area for BTESM and F-BTESM (F/Si = 1/9) Powders Calcined at 350 °C under an Air Atmosphere

|         | surface area (BET) (m² g⁻¹) | pore volume (MP) (cm³ g⁻¹) |
|---------|----------------------------|---------------------------|
| BTESM   | 597                        | 0.34                      |
| F-BTESM (F/Si = 1/9) | 893                        | 0.65                      |

Figure 3b shows the H2O adsorption isotherms at 25 °C for BTESM and F-BTESM (F/Si = 1/9) powders calcined at 350 °C. The amounts of H2O adsorbed onto both samples were normalized by the BET surface area. The adsorbed amounts of H2O on BTESM gel powders increased in an approximately linear fashion with relative pressure increases in the range of 0−0.2, which showed a type III adsorption isotherm. This is because BTESM displays hydrophobic properties by comparison with conventional SiO2 because of the presence of organic linking units (Si−CH2−Si). A similar H2O adsorption property was reported in hydrophobic carbonized-template molecular sieve silica.30 F-BTESM (F/Si = 1/9) gel powder showed a very low amount of H2O adsorption volume, despite having a larger pore volume compared with that of BTESM. Thus, fluorine doping significantly increased the hydrophobic property of organosilica because the density of Si−OH groups in F-BTESM (F/Si = 1/9) was much smaller than that in BTESM.

2.2. Gas Permeation Properties of Fluorine-Doped Organosilica Membranes. Figure 4 shows the molecular size dependence of gas permeance at 200 °C for BTESM and F-BTESM (F/Si = 1/9) membranes calcined at 350 °C. Both membranes showed values for H2 permeance that were higher than 10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹ and permeance ratios for H2/SF6 that were above 1000, which was much higher than the Knudsen ratio (H2/SF6: 8.54). The F-BTESM (F/Si = 1/9) membrane clearly showed lower H2 selectivity (H2/N2, H2/C3H8) compared with that of the BTESM membrane. For example, the F-BTESM (F/Si = 1/9) membrane showed H2/N2 and H2/C3H8 permeance ratios of 4.9 and 11, while those for BTESM were 14 and 690, respectively. The BTESM membrane showed a C3H6 permeance of 2.0 × 10⁻⁸ mol m⁻² s⁻¹ Pa⁻¹ with a C3H6/C3H8 permeance ratio of 13 at 200 °C, which indicated the appropriate network pore size for C3H6/C3H8 separation, as discussed in a previous paper.10 On the other hand, the F-BTESM (F/Si = 1/9) membrane was less selective for C3H6/C3H8 (C3H6/C3H8 permeance ratio: 2.2) because of the enlarged network pore size, which decreased the molecular sieving properties.

Figure 4b shows the molecular size dependence of dimensionless permeance based on He permeance at 200 °C.
for BTESM and F-BTESM (F/Si = 1/9) membranes. The calculated dimensionless permeance based on He under the Knudsen mechanism is shown by the broken lines in the same figure. The dimensionless permeance for a BTESM membrane appeared to roughly follow the range of a Knudsen mechanism for He (0.26 nm) and CO₂ (0.33 nm). The values of dimensionless permeance for molecules larger than N₂ were smaller than those calculated under a Knudsen mechanism, and each value was clearly decreased with increases in the molecular size. On the contrary, the value of dimensionless permeance for the F-BTESM (F/Si = 1/9) membrane was approximately the same as that calculated in the range of He and C₃H₆, which indicated that gas molecules with molecular sizes ranging from 0.26 to 0.5 nm permeated the fluorine-organosilica network structure by Knudsen diffusion. The values of dimensionless permeance for C₃H₈ and SF₆ molecules were smaller than those under Knudsen diffusion, which indicated that molecular sieving dominated the large-molecule permeation. Thus, fluorine doping is viable as a method that can be used to enlarge the network pore sizes of organosilica.

Theoretical analysis was used to estimate the pore sizes of BTESM and F-BTESM (F/Si = 1/9) membranes. Figure S1 shows the relationship between \( k_{0,i}^{1/3} \) and \( d_i \) for BTESM and F-BTESM (F/Si = 1/9) membranes calcined at 350 °C. The pore sizes for BTESM and F-BTESM (F/Si = 1/9) membranes were calculated at 0.49 and 0.62 nm, respectively, based on a modified gas translation model. It should be noted that the average pore size for a F-BTESM (F/Si = 1/9) membrane by nanopermporometry measurement was 0.5 nm.

It is difficult to estimate the membrane quality of microporous membranes with a large network pore size, because molecular sieving only works for large molecules, as shown in Figure 4b. In the present study, the relationship between H₂ permeance and the H₂/SF₆ permeance ratio is generally used as a benchmark for the separation of H₂ over organic compounds such as toluene and methylcyclohexane. Because of the relatively large molecular sizes, the C₃H₆/SF₆ permeance ratio (C₃H₆: 0.468 nm, SF₆: 0.55 nm) was used to estimate the membrane quality.

Figure 5a shows the trade-off curve at 200 °C (H₂ permeance vs H₂/SF₆ permeance ratio) for organosilica (BTESM, BTESE₁⁸,₄,₁¹,₁₄,₃¹ and BTESO₁₄,₃¹), F-BTESM (F/Si = 1/9), and zeolite (DDR, CHA, FAU, and MFI) membranes. The solid line in this figure represents the trade-off between the BTESM and F-BTESM (F/Si = 1/9) membranes. The BTESE (Si-C₂H₄-Si) membranes showed high levels of H₂/SF₆ permeation properties. The BTESO membranes with flexible linking units (Si-C₈H₁₆-Si) showed lower values for H₂ permeance (<10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹), which suggests that increased flexibility is inappropriate for the formation of highly permeable membranes. F-BTESM (F/Si = 1/9) membranes showed higher levels of H₂ permeance with moderate H₂/SF₆ permeance ratios compared with BTESM membranes, but the plotted results fell approximately within the trade-off curve. Thus, the network pore sizes of BTESM and F-BTESM (F/Si
membranes were inadequate for the separation of H₂ over large molecules.

Figure 5b shows the trade-off curve at 200 °C (C₃H₆ permeance vs C₃H₆/SF₆ permeance ratio) for organosilica (BTESM, BTESE¹¹) and F-BTESM (F/Si = 1/9) membranes. In general, the C₃H₆/SF₆ permeance ratio decreases as the C₃H₆ permeance increases because of the presence of interparticle pores in a membrane. The solid line in this figure marks the trade-off for organosilica (BTESM, BTESE¹¹) membranes. F-BTESM (F/Si = 1/9) membranes clearly showed the properties that dictate a high level of C₃H₆/SF₆ permeation. Values for the kinetic diameter³⁶ and L-J length constant³⁷ for hydrocarbon gases (C₃, C₄) lay approximately between the sizes of C₃H₆ (0.468 nm) and SF₆ (0.55 nm), and these are generally used as the effective molecular size for porous media, which makes the network pore size of F-BTESM suitable for the separation of hydrocarbon gases (C₃/C₄, C₄ isomer, etc.).

Figure 6 shows a schematic image of the effect of fluorine doping on an organosilica network structure before/after calcination. As described in the previous section, fluorine doping was present as Si−F and C−F (covalent and semi-ionic, respectively) bonds in the organosilica network. Fluorine doping eliminated the formation of Si−OH groups in the sol, and the condensation of Si−OH groups during the calcination process was suppressed. Wang et al.³⁸ evaluated the effect of calcination temperature (100−300 °C) on the network pore size of organosilica (BTESE) and concluded that He selectivity and the H₂O/alcohol separation factor, corresponding to network pore size, were increased largely as calcination temperature was increased from 100 to 200 °C because of the condensation of Si−OH groups. Thus, the suppression of condensation from the Si−OH groups during the calcination process would have been a factor in the formation of a loose network structure via fluorine doping into organosilica. Because the incorporation of Si−F bonds affected the Si−O−Si bond angle, this change in the organosilica structure

Figure 6. Schematic image of the effect of fluorine doping on an organosilica network structure before/after calcination.

Figure 7. Time course for each permeance and permeance ratio through BTESM (a) and F-BTESM (F/Si = 1/9) (b) membranes in EtOH/H₂O, IPA/H₂O, and n-BuOH/H₂O systems at 70 °C under PV.
could also have helped promote the formation of looser organosilica and F–SiO₂ network structures.¹⁹–²¹

2.3. PV Performance of Fluorine-Doped Organosilica Membranes. Figure 7 shows the time courses for permeance and the permeance ratios through BTESM (a) and F-BTESM (F/Si = 1/9) (b) membranes in EtOH/H₂O, IPA/H₂O, and n-BuOH/H₂O systems at 70 °C under PV. The BTESM membrane showed H₂O permeance of approximately 2.0 × 10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹, irrespective of the separation systems (EtOH/H₂O, IPA/H₂O, and n-BuOH/H₂O), but the permeance of each alcohol was decreased as the molecular size increased (molecular size of alcohol systems: EtOH: 0.43 nm, IPA: 0.47 nm, and n-BuOH: 0.49 nm).³⁹ For example, the permeance values for EtOH, IPA, and n-BuOH through the BTESM membrane were approximately 4.0 × 10⁻⁶, 5.0 × 10⁻⁶, and 3.0 × 10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹, which were approximately 1/50, 1/400, and 1/700 that of H₂O permeance, respectively, and indicated the differences in the molecular sieving mechanisms of these molecules. The permeance values for IPA and n-BuOH reflected their similar molecular sizes.³⁹

PV performances were similar for the F-BTESM (F/Si = 1/9) membrane, and the permeance of H₂O was approximately constant irrespective of the separation system, but the permeance of EtOH was higher than that of either IPA or n-BuOH. It should be noted that organosilica membranes showed stable PV performance, irrespective of fluorine doping, because of the fact that H₂O permeance and each permeance ratio under different separation systems was approximately constant over the course of 10 h at 70 °C.

The permeance values for H₂O, EtOH, IPA, and n-BuOH were plotted as the function of each molecular size together with those of gas molecules at 200 °C, as shown in Figure 8. The permeance of H₂O through the BTESM membrane was higher than that of either He or H₂, despite the larger molecular size. The differences in permeation temperature between single-gas permeation (200 °C) and PV (70 °C) can be explained via the adsorption of H₂O molecules by organosilica.³⁸,⁴⁰,⁴¹ The H₂O molecules adsorbed by organosilica networks permeate via a surface diffusion mechanism. A similar trend was confirmed in BTES (Si–C₃H₆–Si) membranes,³⁸,⁴⁰,⁴¹ which show a hydrophobic nature by comparison with BTESM membranes. The values of EtOH, IPA, and n-BuOH fell approximately within the curve of molecular size dependence for gas permeance at 200 °C.

The F-BTESM (F/Si = 1/9) membrane showed He and H₂ permeance values that were higher than 2.0 × 10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹, which was approximately twice that of the BTESM membrane because of the enlarged network pore size. The H₂O permeance for the F-BTESM (F/Si = 1/9) membrane, however, was approximately the same as that for the BTESM membrane. This result can be explained by the hydrophobic nature of F-BTESM, which impedes H₂O permeation, although the effective molecular size of H₂O was sufficiently small to allow permeation through the loose F-BTESM network. The permeance of H₂O through the F-BTESM (F/Si = 1/9) membrane was lower than that for either He or H₂, which indicates that molecular sieving dominates permeation by H₂O molecules. The F-BTESM (F/Si = 1/9) membrane showed higher values for alcohol permeance by comparison with a BTESM membrane. Because there were no large differences in the alcohol adsorption properties between F-BTESM (F/Si = 1/9) and BTESM, as shown in Figure S2, the increased alcohol permeance through F-BTESM (F/Si = 1/9) could have been caused mainly by decreases in the molecular sieving properties because of loose F-BTESM networks.

3. CONCLUSIONS

Fluorine-doped organosilica membranes for gas/liquid separation were fabricated via a sol–gel method. NH₄F and BTESM were selected as the dopant and Si precursor, respectively, to fabricate fluorine-doped organosilica membranes that were used to evaluate the effect of doped fluorine on the physicochemical properties of organosilica (hydrophobicity/hydrophilicity, network size). Fluorine doping was present as Si–F and C–F (covalent and semi-ionic, respectively) bonds in the organosilica network. Fluorine doping eliminated the formation of Si–OH groups in the sol, so that the condensation of Si–OH groups during the calcination process was suppressed.

Fluorine doping enlarged the network pore sizes of organosilica, and the F-BTESM (F/Si = 1/9) membrane showed He and H₂ permeance that was superior that of a BTESM membrane. The F-BTESM membrane also had a lower H₂/N₂ permeance ratio that corresponded to the network pore size. F-BTESM (F/Si = 1/9) membranes clearly showed high C₃H₆/SF₆ permeation properties (C₃H₆ per-
meance: $>3.0 \times 10^{-7} \text{ mol m}^{-2} \text{s}^{-1} \text{ Pa}^{-1}$, $C_{i}/SF_6$ permeance ratio: $\sim 250$), which shows that the network pore sizes of the F-BTESM are suitable for the separation of hydrocarbon gases ($C_3/C_4$, $C_4$ isomer, etc.).

Organosilica membranes both with and without fluorine doping showed a stable PV performance, and both $H_2O$ permeance and permeance ratios under different separation systems were approximately constant over 10 h at 70 °C. Fluorine doping enhanced the hydrophobic nature of organosilica, which was confirmed by the results of $H_2O$ adsorption and PV.

4. EXPERIMENTAL SECTION

4.1. Preparation of the Fluorine-Doped Organosilica Sol and Membrane Fabrication. A fluorine-doped organosilica sol was prepared via the hydrolysis and polymerization of BTESM with the addition of $NH_4F$ in ethanol with water and $HNO_3$. A specified amount of BTESM and $NH_4F$ was added to ethanol under vigorous stirring at 25 °C [fluorine/Si = 1/9 (molar ratio)]. Then, a specified amount of $HNO_3$ and water was added to maintain the solution composition at a BTESM/$H_2O$/EtOH/$HNO_3$ molar ratio of 1/200/1393/0.1 under a BTESM wt % of 0.5.

Fluorine-doped organosilica membranes were formed onto porous $\alpha$-alumina tubes (porosity: 47%, pore size: 2.1 μm) that were provided by the Nikkato Corporation. First, two types of $\alpha$-alumina particles (average particle diameter: 200 nm, 2 μm) were dispersed in a $SiO_2-ZrO_2$ sol (average sol size: 200 nm) and coated onto the substrate, which was followed by calcination at 550 °C under an air atmosphere in order to form a defect-free intermediate layer. Then, an F-BTESM (F/Si = 1/9) sol diluted to 0.15 wt % was coated onto the intermediate layer, which was followed by calcination at 350 °C under air for 30 min, and then, a mortar was used to grind the dried compound. The $N_2$ and $H_2O$ adsorption isotherms of the organosilica powder were measured at 77 K and 25 °C, respectively (BELMAX, BELJAPAN INC.). The condition of both the fluorine doping in the organosilica structure and that of the fluorine concentration for powdered samples was evaluated via XPS (Thermo Fisher Scientific, ESCALAB 250Xi, Al Ka = 1486.6 eV). A FT-IR spectrometer was used to measure the FT-IR spectra of the films coated onto Si-wafers (FT/IR-4100, Jasco, Japan).

4.2. Preparation and Characterization of Fluorine-Doped Organosilica Films and Gels. Powdered samples of the F-BTESM (F/Si = 1/9) gels were prepared by drying at 40 °C, which was followed by calcination at 350 °C under air for 30 min, and then, a mortar was used to grind the dried compound. The $N_2$ and $H_2O$ adsorption isotherms of the organosilica powder were measured at 77 K and 25 °C, respectively (BELMAX, BELJAPAN INC.). The condition of both the fluorine doping in the organosilica structure and that of the fluorine concentration for powdered samples was evaluated via XPS (Thermo Fisher Scientific, ESCALAB 250Xi, Al Ka = 1486.6 eV). A FT-IR spectrometer was used to measure the FT-IR spectra of the films coated onto Si-wafers (FT/IR-4100, Jasco, Japan).

4.3. Gas Permeation and PV Measurement. Single-gas permeation was conducted using the experimental apparatus shown in Figure 9a.10,14 First, a membrane was pretreated at 300 °C under a $N_2$ flow to remove the chemisorbed water molecules. Pure gases ($He$, $H_2$, $CO_2$, $N_2$, $CH_4$, $C_3H_8$, $C_3H_6$, and $SF_6$) were fed to the outside (upstream) of a cylindrical membrane at 200 kPa, while the permeate side was maintained at atmospheric pressure. An electric furnace controlled the temperature of the permeation cell. A bubble flow meter was used to measure the permeation rate.

The experimental PV apparatus is shown in Figure 9b.43 Fabricated membranes were soaked in an aqueous solution with each alcohol concentration at 90 wt % (water/EtOH, water/IPA, water/BuOH) under a temperature of 70 °C. A reduction in the effect of temperature and concentration polarization on $H_2O$ flux was accomplished by circulating the solution at approximately 1600 rpm. The feed side was maintained at atmospheric pressure, while a vacuum pump (nearly 0 kPa) was used to evacuate the permeate side. A cold trap used liquid nitrogen to collect the permeated vapor, and the compositions of the feed and permeate streams were calculated by gas chromatography using a TCD detector (GC-14B, Shimadzu, Japan; Column: Porapak P). During the PV experiment, water was periodically added to the feed solution to control the concentration of the feed.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01370.

$k_0$ plot for the estimation of network pore size and methanol adsorption isotherm of BTESM and F-BTESM (F/Si = 1/9) powders (PDF)
REFERENCES

Notes

The authors declare no competing financial interest.

(1) Lin, Y. S.; Kumakiri, I.; Nair, B. N.; Alysouri, H. Microporous inorganic membranes. Sep. Purif. Methods 2002, 31, 229–379.

(2) Tsuru, T. Nano/subnano-tuning of porous ceramic membranes for molecular separation. J. Sol-Gel Sci. Technol. 2008, 46, 349–361.

(3) Agirre, I.; Arias, P. L.; Castricum, H. L.; Creatore, M.; ten Elshof, J. E.; Paradis, G. G.; Ngamou, P. H. T.; van Veen, H. M.; Vente, J. F. Hybrid organosilica membranes and processes: Status and outlook. Sep. Purif. Technol. 2014, 121, 2–12.

(4) Caos, G.; Lu, Y.; Delattre, L.; Brinker, C. J.; López, G. P. Amorphous silica molecular sieving membranes by sol-gel processing. Adv. Mater. 1996, 8, 588–591.

(5) Li, G.; Kanezashi, M.; Tsuru, T. Preparation of organic-inorganic hybrid silica membranes using organoalkoxysilanes: The effect of pendant groups. J. Membr. Sci. 2011, 379, 287–295.

(6) Xomeritakis, G.; Tsai, C.-Y.; Brinker, C. J. Microporous sol-gel derived aminosilicate membrane for enhanced carbon dioxide separation. Sep. Purif. Technol. 2005, 42, 249–257.

(7) Paradis, G. G.; Shanahan, D. P.; Kreiter, R.; van Veen, H. M.; Castricum, H. L.; Nijmeijer, A.; Vente, J. F. From hydrophobic to hydrophilic hybrid SiNySi membranes: A change of affinity and applicability. J. Membr. Sci. 2013, 428, 157–162.

(8) Kanezashi, M.; Yada, K.; Yoshioka, T.; Tsuru, T. Design of silica networks for development of highly permeable hydrogen separation membranes with hydrothermal stability. J. Am. Chem. Soc. 2009, 131, 414–415.

(9) Castricum, H. L.; Paradis, G. G.; Mittelmeijer-Hazeleger, M. C.; Kreiter, R.; Vente, J. F.; ten Elshof, J. E. Tailoring the separation behavior of hybrid organosilica membranes by adjusting the structure of the organic bridging group. Adv. Funct. Mater. 2011, 21, 2319–2339.

(10) Kanezashi, M.; Shazwani, W. N.; Yoshioka, T.; Tsuru, T. Separation of propylene/propane binary mixtures by bis(triethoxysilyl) methane (BTESM)-derived silica membranes fabricated at different calcination temperatures. J. Membr. Sci. 2012, 415–416, 478–485.

(11) Niiiri, T.; Nagasawa, H.; Kanezashi, M.; Yoshioka, T.; Ito, K.; Tsuru, T. Preparation of BTES-derived organosilica membranes for catalytic membrane reactors of methylcyclohexane dehydrogenation. J. Membr. Sci. 2014, 453, 375–383.

(12) Castricum, H. L.; Paradis, G. G.; Mittelmeijer-Hazeleger, M. C.; Bras, W.; Eeckhaut, G.; Vente, J. F.; Rothenberg, G.; ten Elshof, J. E. Tuning the nanopore structure and separation behavior of hybrid organosilica membranes. Microporous Mesoporous Mater. 2014, 185, 224–234.

(13) Castricum, H. L.; Qureshi, H. F.; Nijmeijer, A.; Winnubst, L. Hybrid silica membranes with enhanced hydrogen and CO 2 separation properties. J. Membr. Sci. 2015, 488, 121–128.

(14) Kanezashi, M.; Yoneda, Y.; Nagasawa, H.; Tsuru, T.; Yamamoto, K.; Ohshita, J. Gas permeation properties for organosilica membranes with different Si/C ratios and evaluation of microporous structures. AIChE J. 2017, 63, 4491–4498.

(15) Kuwahara, Y.; Kamegawa, T.; Mori, K.; Yamashita, H. Fabrication of hydrophobic zeolites using triethoxyfluorosilane and their application as supports for TiO2 photocatalysts. Chem. Commun. 2008, 4783–4785.

(16) Kuwahara, Y.; Maki, K.; Matsumura, Y.; Kamegawa, T.; Mori, K.; Yamashita, H. Hydrophobic Modification of a Mesoporous Silica Surface Using a Fluorine-Containing Silylation Agent and Its Application as an Advantageous Host Material for the TiO2 Photocatalyst. J. Phys. Chem. C 2009, 113, 1552–1559.

(17) Kosinov, N.; Sripathi, V. G. P.; Hensen, E. J. M. Improving separation performance of high-silica zeolite membranes by surface modification with triethoxyfluorosilane. Microporous Mesoporous Mater. 2014, 194, 24–30.

(18) Kim, Y.-H.; Hwang, M. S.; Kim, H. J.; Kim, J. Y.; Lee, Y. Infrared spectroscopy study of low-dielectric-constant fluorine-incorporated and carbon-incorporated silicon oxide films. J. Appl. Phys. 2001, 90, 3367–3370.

(19) Kanezashi, M.; Matsutani, T.; Wakihara, T.; Tawarayama, H.; Nagasawa, H.; Yoshioka, T.; Okubo, T.; Tsuru, T. Tailoring the Subnano Silica Structure via Fluorine Doping for Development of Highly Permeable CO2 Separation Membranes. ChemNanoMat 2016, 2, 264–267.

(20) Kanezashi, M.; Matsutani, T.; Wakihara, T.; Nagasawa, H.; Okubo, T.; Tsuru, T. Preparation and gas permeation properties of fluorine-silica membranes with controlled amorphous silica structures: Effect of fluorine source and calcination temperature on network size. ACS Appl. Mater. Interfaces 2017, 9, 24625–24633.

(21) Kanezashi, M.; Matsutani, T.; Nagasawa, H.; Tsuru, T. Fluorine-induced microporous silica membranes: Dramatic improvement in hydrothermal stability and pore size controllability for highly permeable propylene/propane separation. J. Membr. Sci. 2018, 549, 111–119.

(22) Grill, A.; Neumayer, D. A. Structure of low dielectric constant to extreme low dielectric constant SiCOH films: Fourier transform infrared spectroscopy characterization. J. Appl. Phys. 2003, 94, 6697–6707.

(23) Parida, S. K.; Dash, S.; Patel, S.; Mishra, B. K. Adsorption of organic molecules on silica surface. Adv. Colloid Interface Sci. 2006, 121, 77–110.

(24) Cao, B.; Tang, Y.; Zhu, C.; Zhang, Z. Synthesis and hydrolysis of hybridized silicon alkoxide: Si(OEt)x(OBut)4-x. Part I: Synthesis and identification of the Si(OEt)x(OBut)4-x. J. Sol-Gel Sci. Technol. 1997, 10, 247–253.

(25) Han, Y.-H.; Taylor, A.; Mantle, M. D.; Knowles, K. M. Sol-gel-derived organic-inorganic hybrid materials. J. Non-Cryst. Solids 2007, 353, 313–320.

(26) Zazzera, L. A.; Moulder, J. F. XPS and SIMS study of anhydrous HF and UV/Ozone-modified silicon (100) surfaces. J. Electrochem. Soc. 1989, 136, 484.

(27) Kawasaki, S.; Komatsu, K.; Okino, F.; Touhara, H.; Katahara, H. Fluorination of open- and closed-end single-walled carbon nanotubes. Phys. Chem. Phys. 2004, 6, 1769–1772.

(28) Lee, J.-M.; Kim, S. J.; Kim, J. W.; Kang, P. H.; Nho, Y. C.; Lee, Y.-S. A high resolution XPS study of sidewall functionalized MWCNTs by fluorination. J. Ind. Eng. Chem. 2009, 15, 66–71.

(29) Erdey, L.; Gál, S.; Liptay, G. Thermoanalytical properties of analytical-grade reagents. Talanta 1964, 11, 913–940.

(30) Duke, M. C.; da Costa, J. C. D.; Do, D. D.; Gray, P. G.; Lu, G. Q. Hydrothermally robust molecular sieve silica for wet gas separation. Adv. Funct. Mater. 2006, 16, 1215–1220.

(31) Ren, X.; Kanezashi, M.; Nagasawa, H.; Tsuru, T. Preparation of organosilica membranes on hydrophobic intermediate layers and evaluation of gas permeation in the presence of water vapor. J. Membr. Sci. 2015, 496, 156–164.

(32) Bai, C.; Jia, M.-D.; Falconer, J. L.; Noble, R. D. Preparation and separation properties of silicate composite membranes. J. Membr. Sci. 1995, 105, 79–87.

(33) Kanezashi, M.; O’Brien-Abraham, J.; Lin, Y. S.; Suzuki, K. Gas permeation through DDR-type zeolite membranes at high temperatures. AIChE J. 2008, 54, 1478–1486.

(34) Kosinov, N.; Auffret, C.; Sripathi, V. G. P.; Gücüyener, C.; Gascon, J.; Kapteijn, F.; Hensen, E. J. M. Influence of support morphology on the detemplation and permeation of ZSM-5 and SSZ-
13 zeolite membranes. Microporous Mesoporous Mater. 2014, 197, 268−277.

(35) Zhou, C.; Yuan, C.; Zhu, Y.; Caro, J.; Huang, A. Facile synthesis of zeolite FAU molecular sieve membranes on bio-adhesive polydopamine modified Al2O3 tubes. J. Membr. Sci. 2015, 494, 174−181.

(36) Breck, D. W. In Zeolite Molecular Sieves, Structure, Chemistry and Use; Fla, M., Krieger, R. E., Eds.; John Wiley: New York, 1974; pp 1−771.

(37) Hirchfelder, J. H.; Curtiss, C. F.; Bird, R. B. Molecular Theory of Gases and Liquids, 2nd ed.; Wily: New York, 1964; pp 1109–1180.

(38) Wang, J.; Kanezashi, M.; Yoshioka, T.; Tsuru, T. Effect of calcination temperature on the PV dehydration performance of alcohol aqueous solutions through BTESE-derived silica membranes. J. Membr. Sci. 2012, 415−416, 810−815.

(39) Tokay, B.; Falconer, J. L.; Noble, R. D. Alcohol and water adsorption and capillary condensation in MFI zeolite membranes. J. Membr. Sci. 2009, 334, 23−29.

(40) Xu, R.; Wang, J.; Kanezashi, M.; Yoshioka, T.; Tsuru, T. Reverse osmosis performance of organosilica membranes and comparison with the pervaporation and gas permeation properties. AIChE J. 2013, 59, 1298−1307.

(41) Nagasawa, H.; Matsuda, N.; Kanezashi, M.; Yoshioka, T.; Tsuru, T. Pervaporation and vapor permeation characteristics of BTESE-derived organosilica membranes and their long-term stability in a high-water-content IPA/water mixture. J. Membr. Sci. 2016, 498, 336−344.

(42) Asaeda, M.; Okazaki, K.; Nakatani, A. Preparation of thin porous silica membranes for separation of non-aqueous organic solvents mixtures by pervaporation. Ceram. Trans. 1992, 31, 411−420.

(43) Wang, J.; Tsuru, T. Cobalt-doped silica membranes for pervaporation dehydration of ethanol/water solutions. J. Membr. Sci. 2011, 369, 13−19.