Tailoring a Thermally Stable Amorphous SiOC Structure for the Separation of Large Molecules: The Effect of Calcination Temperature on SiOC Structures and Gas Permeation Properties

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Supporting Information

ABSTRACT: A SiOC membrane with high oxidative stability for gas separation was tailored by utilizing vinyltrimethoxysilane, triethoxysilane, and 1,1,3,3-tetramethyldisiloxane as Si precursors. Amorphous SiOC networks were formed via the condensation of Si–OH groups, the hydrosilylation of Si–H and Si–CH═CH2 groups, and a crosslinking reaction of Si–CH2 groups, respectively. The crosslinking of Si–CH2 groups at temperatures ranging from 600 to 700 °C under a N2 atmosphere was quite effective in constructing a Si–CH2═Si unit without the formation of mesopores, which was confirmed by the results of N2 adsorption and by the gas permeation properties. The network pore size of the SiOC membrane calcined at 700 °C under N2 showed high oxidative stability at 500 °C and was appropriate for the separation of large molecules (H2/CF4 selectivity: 640, H2/SF6: 2900, N2/CF4: 98). A SiOC membrane calcined at 800 °C showed H2/N2 selectivity of 62, which was approximately 10 times higher than that calcined at 700 °C because the SiOC networks were densified by the cleavage and redistribution reactions of Si–C and Si–O groups.

INTRODUCTION

A simple, energy-conserving, high-performance separation system is possible via membrane-based separation (permeance, selectivity, and stability). This process has the potential to replace conventional separation processes, such as distillation and adsorption. Thus, many types of materials have been used in membrane development: polymer,1,2 zeolite,3,4 amorphous silica,5,6 and carbon molecular sieves.8,9 Amorphous silica membranes have been studied intensively due to a microporous structure that can withstand 1000 °C with a high degree of chemical stability. However, the network pore sizes of conventional amorphous SiO2 membranes are only suitable for the separation of small molecules such as H2/N2 and H2/CH4, and silica networks are easily densified under a hydrothermal atmosphere, which results from the condensation of Si–OH groups, particularly at high temperatures.10,11

The ability to introduce organic functional groups into an amorphous silica structure enlarges the network pore size, which improves hydrothermal stability.12–14 These attributes make the silicon oxyxycarbide (SiOC) structure a good candidate for tailoring the pore size of a network with a high degree of stability. The SiOC structure is generally derived from the SiC structure in polydimethylsilane (PMS),13–17 polycarboxilane,18–22 and polysilastrene,23 followed by electron beam irradiation20,22 and oxidation curing.6–19 Lee and Tsai24 evaluated the effect of heat treatment on the gas permeation properties of SiOC membranes, which were prepared via the pyrolysis of PMS at temperatures ranging from 300 to 600 °C under an Ar atmosphere. A SiOC membrane fabricated at 600 °C showed H2 permeance of 4.9 × 10−9 mol m−2 s−1 Pa−1 with a H2/N2 permeance ratio of 41 at 200 °C. A trend was confirmed whereby H2 permeance is largely decreased as the temperature of heat treatment increases due to a densification of the PMS structures. The optimization of pyrolysis conditions can be used to tailor the thermally stable SiOC networks for H2 separation, but further efforts are required to tailor a looser network structure.

In 2014, our research group fabricated SiOC membranes by utilizing triethoxysilane (TRIES), vinyltrimethoxysilane (VTMS), and 1,1,3,3-tetramethyldisiloxane (TMDSO) as Si precursors via sol–gel processing.24 A SiOC membrane calcined at 400 °C under a N2 atmosphere showed a loose network structure, but the chemical structure and gas permeation properties of SiOC membranes calcined at high temperatures have not been verified. Several papers have reported the introduction of Si–CH2═Si units via a cross-linking of the Si–CH2 groups above 600 °C under an Ar atmosphere, and surprisingly these studies reported no change in the SiOC structures that were created even after calcination at 900 °C.25 However, no study has focused on tailoring the...
SiOC structure for use in a molecular sieving membrane via a crosslinking of the Si−CH₃ groups at high temperature.

In the present study, a SiOC network structure with high oxidative stability for gas separation was tailored by utilizing VTMS, TRIES, and TMDSO as Si precursors. Figure 1 shows a schematic image of the formation of an amorphous SiOC structure. First, silsesquioxane (SQ, RSiO₁.₅) networks were formed by the hydrolysis and polymerization reactions of VTMS and TRIES. Then, TMDSO was introduced into SQ networks via hydrosilylation. After gelation of the film, crosslinking reactions of Si−CH₃ groups at high temperatures were conducted to control the network pore size for gas separation. The effects of calcination temperatures on the SiOC network structures and on the gas permeation properties of SiOC membranes were evaluated according to single-gas permeation properties. The oxidative stability of SiOC membranes was also evaluated by measuring the time courses of gas permeance during air treatment at 500 °C. The SiOC structure was characterized via solid-state NMR, Fourier transform infrared (FT-IR), and N₂ adsorption experiments.

**RESULTS AND DISCUSSION**

**Characterizing the SiOC Structure.** In the present study, a Pt catalyst was added to the SQ sol derived from TRIES and VTMS to introduce TMDSO into the SQ network via hydrosilylation. The effect of the Pt catalyst on the reactivity of the Si−H groups in TMDSO was evaluated via FT-IR. Figure 2 shows the FT-IR spectra ranging from 500 to 4000 cm⁻¹ for uncalcined SiOC films, which were prepared by coating SiOC sols with/without a Pt catalyst onto a Si wafer.

The antisymmetric stretching vibration bonds of Si−O−Si (νₛ) appeared between 1000 and 1150 cm⁻¹ for both samples, which indicated that the hydrolysis and condensation reactions had formed siloxane networks regardless of the absence or presence of a Pt catalyst. The two split peaks appearing at 2100 and 2320 cm⁻¹ were assigned to the Si−H symmetric stretching vibration bonds (νₛ Si−H). The Si−H peaks that appeared at 2250 and 2140 cm⁻¹ were derived from TRIES and TMDSO, respectively. The SiOC film prepared from the sol without a Pt catalyst showed two types of Si−H peaks, whereas that with a Pt...
catalyst showed a weak Si–H peak derived from TMDSO. Peaks at 1600 and 1410 cm\(^{-1}\) assigned to Si–C==C stretching vibration bonds (\(\nu\) Si–C==C)\(^{34}\) were decreased in the film prepared with a Pt catalyst. Thus, we concluded that the hydrolysilation of Si–H groups and Si–C==C groups in eq 1 had proceeded with the addition of a Pt catalyst to the SiO sol at a low temperature (40 °C or less).\(^{35}\)

\[
\text{Si–H + Si–C==C \rightarrow Si–C=H–Si}
\]

Since the Si–C==C groups in VTMS and the TRIES-derived Si–H groups in TRIES–VTMS hybrid polymers are located separately via the formation of Si–O–Si bonds caused by the hydrolysis and condensation of Si–OCH\(_3\) and Si–OC\(_2\)H\(_5\) groups, the reactivity of intermolecular hydrosilylation between the Si–C==C groups in VTMS and the TRIES-derived Si–H groups might be low. TMDSO can only be introduced in the atmosphere (ramping rate, 10 \(\text{mL min}^{-1}\)) from the methoxy and ethoxy groups, respectively.\(^{26,33,36}\) These had proceeded with the addition of a Pt catalyst to the SQ sol at the hydrosilylation of Si groups prepared with a Pt catalyst. Thus, we concluded that the crosslinking reactions of Si–CH\(_3\) groups expressed in eqs 2 and 3 occurred at 600 and 800 °C, respectively, under an inert atmosphere.\(^{35,31,38–41}\)

\[
\begin{align*}
\text{Si–CH}_3 + \text{Si–H} & \rightarrow \text{Si–CH}_2–\text{Si} + \text{H}_2 \quad (2) \\
\text{Si–CH}_3 + \text{Si–CH}_3 & \rightarrow \text{Si–CH}_2–\text{Si} + \text{CH}_4 \quad (3)
\end{align*}
\]

The SiOC gel showed no weight loss at temperatures ranging from 800 to 1000 °C, which indicated a completion of the related reactions and decomposition of the crosslinking units. The SiOC gel showed a residual weight of approximately 90% even after heat treatment at 1000 °C.

Figure 4 shows the solid-state \(^{13}\)C cross-polarization magic-angle-spinning (CP MAS) NMR signals of SiOC gels ranging from −50 to 250 ppm (a) and a highly magnified version that ranged from −15 to 15 ppm (b). The signal detected at 6.0 ppm of uncoked gel was assigned to Si–C=H–Si linking units\(^{12–44}\) that were formed via hydrosilylation with a Pt catalyst. Another intense signal at approximately 0.3 ppm that corresponded to the −CH\(_3\) groups derived from TMDSO\(^{40,45}\) was detected in uncoked gel.

These signals showed no differences when a sample was calcined below 500 °C, but a downfield signal shift occurred when the temperature was raised above 600 °C. The sample calcined at 600 °C showed an intense signal at −0.6 ppm that was assigned to the −CH\(_3\)– groups in the Si–CH\(_2–\)Si–linking units\(^{36,45}\) and was caused by the crosslinking reaction of Si–CH\(_3\) groups, as expressed in eqs 2 and 3. The signal at 6.0 ppm that was assigned to the Si–C=H–Si unit was decreased above 600 °C due to cleavage of the Si–C=H–Si unit.

The sample calcined at 800 °C showed a signal at −7.6 ppm that was assigned to the Si–CH\(_3\) groups formed by the cleavage of crosslinking units.\(^{47}\) The broad signal at around 130 ppm with spinning side bands (176 and 84 ppm) was assigned to the aromatic carbon atoms\(^{43,48,49}\) and the formation of a free-carbon phase at 800 °C was indicated by the partial decomposition of Si–CH\(_3\) groups and/or organic linking units.\(^{47}\)

Figure 5 shows the solid-state \(^{29}\)Si MAS NMR spectra of SiOC gels using the same samples measured for the \(^{13}\)C CP MAS NMR spectra. The signals appearing at approximately −17.1, −65.5, −101, and −110 ppm in the uncaked sample can be ascribed to (Si\(_2\)C\(_2\))\(_2\)O (D\(_{\text{TMDSO}}\) unit), SiO\(_2\)C (T unit),\(^{39,47}\) SiO\(_2\)(OH) (Q\(_3\) unit),\(^{51}\) and SiO\(_4\) (Q\(_4\) unit).\(^{39,47}\)respectively. The ratio of the Q\(_3\) unit decreased as the temperature increased from the condensation of Si–OH groups. The signals of Si–CH\(_3\) groups decreased when a sample was calcined at 700 °C and almost disappeared at 800 °C. In the same temperature range, however, the signals of T units increased.

The peak areas of the ratios for D\(_{\text{TMDSO}}\) and T units at each heat-treated temperature are summarized in Table 1. Gaussian distribution fitting was used to conduct the deconvolution in each peak. The peak area ratio of D\(_{\text{TMDSO}}\) units was defined as D\(_{\text{TMDSO}}\)/[Q + T + D\(_{\text{TMDSO}}\)] in the SiOC structure, and the ratio decreased with increase in the calcination temperature. The difference in the peak area ratio of T units was defined as T/(Q + T + D\(_{\text{TMDSO}}\)), and this value was small for samples calcined below 700 °C. The peak area ratio of T units was increased, however, when a sample was calcined at 800 °C. In their study, Babonneau et al.\(^{41}\) noted a similar phenomenon wherein D units (Si\(_2\)O\(_4\)?C\(_2\)) in the SiOC structure derived from
tetraethoxysilane (Si(OEt)$_4$) and diethoxydimethylsilane ((CH$_3$)$_2$Si(OEt)$_2$) changed to T units, which was caused by the cleavage and redistribution reaction of Si–C and Si–O bonds$^{39,52-55}$ during heat treatment under temperatures that ranged from 400 to 600 °C under an argon atmosphere.

**Effect of Calcination Temperatures on Microporous Structure and Gas Permeation Properties.** Figure 6 shows the N$_2$ adsorption isotherms at 77 K (a) and the specific surface areas as a function of calcination temperature (500–800 °C) (b). The specific surface areas for SiOC gels were calculated using the Brunauer–Emmett–Teller (BET) method for relative pressures ($p/p_0$) ranging from 0.1 to 0.3.

The adsorption isotherm of uncalcined gel showed low nitrogen adsorption volumes and resembled a type II isotherm. The introduction of TMDSO into the networks could have acted as a “large pendant” unit, which could have blocked micropore access by N$_2$, which would suggest nonporous properties. The SiOC gel samples calcined above 500 °C, however, showed highly adsorbed volumes at low relative pressures and large increases in the specific surface areas. The volume of adsorbed N$_2$ for the SiOC sample calcined at 500 °C continued to increase in relative pressures that ranged from 0.1 to 1.0, suggesting the presence of mesopores. Table 2 summarizes the pore volume of uncalcined and calcined SiOC gels (500–800 °C, N$_2$ atmosphere) via the micropore (MP) analysis and Barrett–Joyner–Halenda (BJH) methods. Mesopore volume using the BJH method clearly decreased as heat treatment temperatures increased from 500 to 600 °C. This was likely caused by the crosslinking reaction of Si–CH$_3$ groups in TMDSO, which would have resulted in a decrease in the formation of mesopores. There was no large difference in micropore volume using the MP method for SiOC gels calcined at 500–700 °C, and a SiOC gel calcined at 800 °C showed the smallest pore volume. This was likely caused by a densification of the SiOC structure that resulted from a redistribution of the Si–C and Si–O bonds$^{39,52-55}$.

Table 1. Peak Area Ratios of D$_{TMDSO}$ Units and T Units for Both Uncalcined and Calcined SiOC Gels (500–800 °C, N$_2$ Atmosphere) Using Gaussian Distribution Fitting

| calcination condition | $D_{TMDSO}/(Q + T + D_{TMDSO})$ | $T/(Q + T + D_{TMDSO})$ |
|-----------------------|----------------------------------|--------------------------|
| uncalcined gel        | 0.34                             | 0.16                     |
| 500 °C                | 0.35                             | 0.18                     |
| 600 °C                | 0.25                             | 0.21                     |
| 700 °C                | 0.13                             | 0.26                     |
| 800 °C                | 0.41                             | 0.41                     |

Figure 7 shows the gas permeance at 200 °C as a function of the molecular size for SiOC membranes calcined at 500–800
A SiOC membrane calcined at 500 °C under a N2 atmosphere. A SiOC membrane calcined at 500–700 °C showed approximately the same levels of permeance for He, H2, CO2, and N2, irrespective of the calcination temperature. For example, a SiOC membrane calcined at 500 °C showed high H2 permeance of 8.9 × 10−7 mol m−2 s−1 Pa−1 with H2/N2, H2/CF4, H2/SF6 selectivities of 5.9, 240, and 1400, respectively. Figure S1 shows the temperature dependence of gas permeance for a SiOC membrane calcined at 500 °C under a N2 atmosphere. The permeances of He and H2 were approximately independent of temperature, and N2, CH4, CF4, and SF6 molecules showed the Knudsen-type permeation behavior; permeance slightly increased with decreasing temperature. The permeance of CO2 increased with decreasing temperature, which is a surface diffusion mechanism, since CO2 molecules are adsorptive and have a strong affinity with the SiOC structure.24 Gas selectivity for small molecules (H2/N2 selectivity: 5.9) was controlled by the Knudsen diffusion through network pores and for large molecules (H2/CF4: 240, H2/SF6: 1400) by molecular sieving.24 A SiOC membrane calcined at 700 °C showed smaller values for CH4, CF4, and SF6 permeances compared with that calcined at 500 °C; a SiOC membrane calcined at 700 °C showed higher selectivity for large molecules (N2/CF4: 98; H2/CF4: 640; H2/SF6: 2900).

Organic crosslinking reactions of Si–CH3 groups occurred when a membrane was heat-treated at 700 °C under a N2 atmosphere, and the formation of SiOC networks via organic crosslinking reactions decreased the occurrence of mesopores that CF4 and SF6 are able to permeate, which narrowed the pore size distribution. This trend was consistent with the elimination of mesopores in the SiOC structure via organic crosslinking reactions based on the results of N2 adsorption property. A SiOC membrane calcined at 800 °C showed smaller values of He and H2 permeances compared with that calcined at 500–700 °C, which demonstrated that He permeance was higher than that of H2. A SiOC membrane calcined at 800 °C showed H2/N2 selectivity of 62, which was approximately 10 times higher than that calcined at 700 °C due to the densification of SiOC networks.

Figure 8 shows a schematic image of the formation of a SiOC network and the effect of calcination temperature on a SiOC network. First, TMDSO was introduced into the SQ networks via the hydrosilylation of Si–H and Si–C=C groups. No significant change was noted in the chemical structure of the SiOC network, however, before heat treatment at 500 °C. Then, when heat treatment reached 600–700 °C, a crosslinking of Si–CH3 groups occurred, which is known to prevent the formation of mesopores based on the results of N2 adsorption and gas permeation properties. At higher temperatures (>800 °C), a free-carbon phase was formed by the partial decomposition of organic groups,38,44 and the SiOC structure began to densify, which likely was a result of the cleavage and redistribution reactions of the Si–C and Si–O groups.39,52–55

### Evaluating the Oxidative Stability and Structure of an SiOC Membrane.

Figure 9 shows the time courses of single-gas permeance and gas selectivities (He/N2 and N2/CF4) for the SiOC membrane calcined at 700 °C during exposure to air.

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**Table 2. Pore Volume of Uncalcined and Calcined SiOC Gels (500–800 °C, N2 Atmosphere) via the MP and BJH Methods**

| calcination condition | MP method | BJH method |
|-----------------------|-----------|------------|
| uncalcined gel        | 0.008     | 0.017      |
| 500 °C                | 0.205     | 0.061      |
| 600 °C                | 0.187     | 0.038      |
| 700 °C                | 0.183     | 0.027      |
| 800 °C                | 0.122     | 0.020      |

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**Figure 6.** N2 adsorption isotherms at 77 K (closed symbols: adsorption, open symbols: desorption) (a) and the specific surface areas calculated using the BET method as a function of calcination temperature (b).

**Figure 7.** Molecular size dependence of gas permeance at 200 °C for SiOC membranes calcined at 500–800 °C under a N2 atmosphere.
at 500 °C. Molecular size dependence on gas permeance at 200 °C before/after air treatment (500 °C, 15 h) is shown in Figure 10. Although the value of each permeance gradually increased in the initial stages of exposure to air, each permeance reached a steady state after exposure to air for 15 h. Air-treated SiOC membranes showed high selectivity for large molecules. For example, the permeance of N₂ increased slightly from $8.9 \times 10^{-8}$ to $1.1 \times 10^{-7}$ mol m⁻² s⁻¹ Pa⁻¹ with a slight decrease in N₂/CF₄ selectivity from 66 to 49, confirming the oxidative stability of the SiOC structure for the separation of large molecules.

Following air treatment, SiOC membranes showed a trend whereby the values for permeance of gas with a large molecular size increased significantly compared with gases of smaller molecular size. This is because large molecules, such as CF₄ and SF₆, could only permeate large pores (few grain boundaries) in the membranes before air treatment. As described in Experimental Section, in the present study, an amorphous SiOC layer was fabricated on the SiO₂−ZrO₂ intermediate layer with a pore size distribution in the range of 1–5 nm. Thus, SQ sol cannot completely cover large pores in the intermediate layer, resulting in the formation of a few large spaces with pore sizes larger than 0.6 nm (grain boundaries), where CF₄ and SF₆ can permeate via the Knudsen diffusion.

Even though SiOC networks were quite stable against an oxidative atmosphere, the partial oxidation of Si−CH₃ groups enlarged the SiOC network, which could have decreased the level of molecular sieving for larger molecules. Small molecules, such as He and H₂, easily permeate loose SiOC networks, irrespective of air treatment, so that the ratio of He and H₂ permeance was less affected by air treatment.

Figure 11 shows the solid-state $^{29}$Si MAS-NMR spectra of a SiOC gel calcined at 700 °C before/after air treatment at 500 °C. The decrease in D units could have been caused by the oxidation of Si−CH₃ to SiO₂, which would be consistent with the increased gas permeance during the initial stage of exposure to air. On the other hand, there were no large changes in T units even after air treatment, which indicates the oxidative stability of the resultant SiOC structure. The peak ratios of D units ($D_{TMSO}/(Q + T + D_{TMSO})$) and T units ($T/(Q + T + D_{TMSO})$) were 0.07 and 0.26, respectively, and there was no change in the T peak ratio of the SiOC gels before/after air treatment.
CONCLUSIONS
A SiOC membrane with high oxidative stability for gas separation was tailored by utilizing VTMS, TRIES, and TMDSO as Si precursors. Amorphous SiOC networks were formed by the condensation of Si−OH groups via hydrolysilation of Si−H and Si−CH=CH2 groups and by the crosslinking reaction of Si−CH3 groups. The effects of calcination temperatures on the SiOC network structure and on the gas permeation properties of SiOC membranes were evaluated, and the oxidative stability of SiOC membranes was evaluated by measuring the time courses of gas permeance during air treatments at 500 °C.

The results of N2 adsorption and gas permeation properties showed that the crosslinking of Si−CH3 groups at temperatures ranging from 600 to 700 °C under a N2 atmosphere during the formation of the Si−CH2−Si unit were quite effective in preventing the formation of mesopores. The network pore sizes in SiOC membranes calcined at 700 °C were appropriate for the separation of large molecules (H2/CF4 selectivity: 640, H2/SF6: 2900, N2/CF4: 98). A SiOC membrane calcined at 800 °C showed H2/N2 selectivity of 62, which was approximately 10 times higher than that calcined at 700 °C because of the densification of SiOC networks caused by the cleavage and redistribution reactions of Si−C and Si−O groups.

A SiOC membrane calcined at 700 °C showed oxidative stability at 500 °C because the differences were insignificant for molecular sieving properties before/after air treatment at 500 °C for 15 h. Each permeance value gradually increased during the initial stages of exposure to air, but a steady state was reached after exposure to air for 15 h.

EXPERIMENTAL SECTION
Preparation of the SiOC Sol and Membranes. The SiOC sol was prepared via the following process. First, SQ networks were formed by subjecting VTMS and TRIES to hydrolysis and polymerization reactions via the sol−gel method. VTMS and TRIES were dissolved in isopropyl alcohol (IPA) and hydrolyzed with water and HCl diluted by IPA and then stirred for 1 h at 50 °C. Then, TMDSO was introduced into the SQ networks via hydrolysilation at 25 °C for 1 h using a mixture of hydrogen hexachloroplatinate(IV) hexahydrate (H2PtCl6·6H2O) as a catalyst. The molar ratio of the Si precursors and the mixture was VTMS/TRIES/TMDSO = 1:3:1 and Si/H2O/HCl/Pt = 1:120:0.1:1.6 × 10−3, with the Si precursor maintained at 3.0 wt %.

SiOC membranes were fabricated using porous α-alumina tubes (porosity, 50%; average pore size, 1 μm; outside diameter, 10 mm; tube length, 100 mm, Nikkato, Co., Japan). First, an α-alumina particle layer was fabricated by coating two types of α-alumina particles (large particles, 2.7 μm; small particles, 0.2 μm) with SiO2−ZrO2 (Si/Zr = 1:1) colloidal sols as a binder to smooth the surface of the porous α-alumina tubes. The intermediate layer was then fabricated by coating SiO2–ZrO2 (Si/Zr = 1:1) colloidal sols onto the α-alumina layer with calcination at 500−800 °C under an air atmosphere for 10 min. Finally, to promote gas separation, the top layer amounted to a coating of the SiOC sol followed by...
calcination at 500–800 °C for 30 min under a nitrogen atmosphere.

Characterization of SiOC Films and Gels. Fourier transform infrared (FT-IR) measurement of the SiOC films coated onto a silicon wafer was conducted at room temperature using a FT-IR spectrometer (FT/IR-4100, Jasco, Co., Japan). SiOC gel powders were prepared by drying at 40 °C under an air atmosphere and were calcined at 500–800 °C under nitrogen for 1 h. Thermogravimetric-mass spectrometric (TG-MS) analysis was performed via TG-MS (TG-DTA-410S, Rigaku Co., Japan) under a helium atmosphere, and the temperature was ramped up at a rate of 10 °C min⁻¹ to a level of 1000 °C. Before TG analysis, the sample was maintained at 150 °C under a helium atmosphere at a flow rate of 300 mL min⁻¹ for 2 h to remove the adsorbed water. The N₂ adsorption isotherms for SiOC gels were measured at 77 K using a BELMAX (BELL Co., Japan). Prior to N₂ adsorption measurement, the uncalcined SiOC gel was pretreated at 100 °C under vacuum for 24 h, and SiOC gels calcined at 500–800 °C were pretreated at 200 °C under vacuum for 12 h.

Solid-state ¹³C CP MAS-NMR, and ²⁹Si MAS-NMR were recorded using a NMR spectrometer (Varian 600PS, Agilent Inc.). ¹³C CP MAS-NMR measurements were conducted at 150.9 MHz using ¹³C−¹H dipolar couplings. The spectra were acquired with a 90° pulse of 3.2 μs with the recycle delay set at 70 s for 360 scans. The peak position was referenced to the signal of hexamethylbenzene. A 6 mm diameter zirconia rotor spun at 7 kHz. ²⁹Si MAS-NMR measurements were conducted at 119.2 MHz with the recycle delay set at 70 s for 400 scans. The peak position was chosen in reference to the signal of 3- (trimethylsilyl)proplionic acid carboxylic acid sodium salt. The ²⁹Si NMR spectra were also obtained using a 6 mm diameter zirconia rotor spun at 7 kHz.

Single-Gas Permeation Measurement and Testing for Oxidation Stability. Single-gas permeation (50–500 °C) and oxidative stability measurements of SiOC membranes were performed using the experimental apparatus shown in Figure 12. High-pure, single-probe gases (He, H₂, CO₂, N₂, CH₄, CF₄, and SF₆) were fed to the outside (upstream) of the membrane at atmospheric pressure, and the permeate side (downstream) was evacuated using a vacuum pump. Each permeance value was calculated using the observed pressure difference between the upstream and downstream values of the membrane, and the permeation rate was obtained via a calibrated critical nozzle located between the permeation cell and a vacuum pump.

The oxidative stability of the SiOC membrane was evaluated by measuring the time course of gas permeance (He, N₂, CH₄, and CF₄) at 500 °C during air treatment. The air treatment was conducted at 500 °C by feeding air into the membrane module for a specified time interval, and the changes were noted for each level of permeance during the air treatment.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00632.

Temperature dependence of gas permeances for a SiOC membrane calcined at 500 °C in N₂ atmosphere (Figure S1) (PDF)
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