Zeolite membranes can be used for separation and purification of natural gas. Natural gas contains mainly methane and carbon dioxide, but also contains acidic gases, such as hydrogen sulfide, and water. The application of conventional zeolite membranes containing aluminum to these separation processes is difficult because of poor acid durability and reduced flux in the presence of water. Pure silica zeolite membranes have high acid stability and are hydrophobic. In this study, STT-type zeolite was chosen as a membrane material for the relatively high pore volume and pure silica STT-type zeolite can be prepared. STT-type zeolite was milled in a ball mill for 8 h, and then coated on a porous alumina substrate. STT-type zeolite membranes were prepared by the secondary growth method. Times for synthesis of the STT-type zeolite particles and ball milling were optimized. The effects on permeance of synthesis time, and of the structure-directing agent/SiO2 and H2O/SiO2 ratios for secondary growth were investigated. STT-type zeolite membrane prepared from gel with a mole ratio of 1.0 SiO2 : 0.25 N,N,N-trimethyl-1-adamantane ammonium hydroxide : 54 H2O with hydrothermal synthesis for 8 days at 150 °C had high permeance ratio (169) for hydrogen to sulfur hexafluoride (SF6).

Keywords
STT type zeolite, Membrane, Pure silica, Gas separation, Natural gas

1. Introduction

Membrane separation has a number of distinct advantages over the conventional separation techniques of pressure swing adsorption (PSA) and distillation, such as continuous operation, low investment cost, low energy consumption, and cost effectiveness. Zeolite membrane materials have been widely investigated because of their uniform pore sizes and high pore volumes (1-3). Zeolites generally contain silicon (Si), aluminum (Al), oxygen, and cations, such as protons, sodium ions, or calcium ions. The Si/Al ratio of the zeolite affects the physicochemical properties, and the hydrophobicity, thermal stability, and acid tolerance increase with higher Si/Al ratio (4,5). In addition, the number of cations in the zeolite framework decreases and the pore volume increases with lower Al content. Consequently, zeolite membrane with high Si/Al ratio provides superior mass transfer compared to zeolite membrane with low Si/Al ratio. The characteristics of mass transfer affect the membrane permeance and selectivity (5). Therefore, many studies have investigated the preparation and characterization of zeolite membranes with high Si/Al ratios (5-7).

Pure silica zeolites (Si/Al ratio of infinity) have been extensively investigated as carbon dioxide (CO2) permselective membrane materials for natural gas purification. Natural gas contains minor gas components such as hydrogen sulfide (H2S) and water, and major gas components such as methane (CH4) and CO2. Water and H2S are preferentially adsorbed by the aluminum in the zeolite framework, leading to reduced CO2 separation performance (8). Pure silica zeolites include chabazite (CHA-type zeolite), deca-dodecasil 3R (DDR-type zeolite), silicalite-1 (MFI-type zeolite), beta (BEA-type zeolite), and SSZ-23 (STT-type zeolite) (9-13). STT-type zeolites have relatively high pore volumes among these zeolites, and so are expected to form membranes with high gas diffusion (13). STT-type zeolites have nine-membered (0.37 × 0.53 nm) and seven-membered ring windows (0.25 × 0.35 nm), which allow for permeation of helium (He, kinetic diameter: 0.28 nm), hydrogen (H2, 0.29 nm), and CO2 (0.33 nm) (14). However, preparation of STT-type zeolite membranes has rarely been reported. Pure silica STT-type zeolite (Si-STT) membrane was prepared by Kida et al. (9). However, the effects of the synthesis time, water, and structure-directing agent (SDA) on the membrane preparation were not clear. In addition, scale-up of this membrane preparation process could be difficult because it was pre-
pared from a highly viscous secondary growth gel with low water content.

In this study, STT-type zeolite membranes were prepared and the effects of secondary growth conditions (synthesis time, $\text{H}_2\text{O}/\text{SiO}_2$, and SDA/\text{SiO}_2) were investigated on the gas permeation properties.

2. Experimental

2.1. Synthesis of Si-STT Seed Crystals

Si-STT seed crystals were prepared by hydrothermal synthesis\(^{(10)}\). Tetraethyl orthosilicate (Wako Pure Chemical Industries, Ltd.) and $N,N,N$-trimethyl-1-adamantane ammonium hydroxide (TMAdaOH, Sachem), which was used as a SDA, were mixed and kept overnight under gentle stirring (250 rpm). Then, the mixture was heated to evaporate the water and ethanol formed by polycondensation of tetraethyl orthosilicate. The obtained solid product was crushed in an agate mortar and pestle, and 46 wt% hydrofluoric acid aqueous solution (Wako Pure Chemical Industries, Ltd.) was added. Water was evaporated to obtain a mole ratio of $\text{SiO}_2 : \text{TMAdaOH} : \text{HF} : \text{H}_2\text{O}$ of 1.0 : 0.50 : 0.50 : 7.5. The obtained gel was treated in a Teflon-lined stainless-steel autoclave at 150 °C for 3-9 days. Then, the autoclave was removed from the oven and cooled to room temperature, and the product was recovered by filtration, washed with distilled water, and dried under reduced pressure for 24 h. The samples were characterized by X-ray diffraction (XRD, RINT TTR3, Rigaku Corp.), field emission scanning electron microscope (FE-SEM, S-4800, Hitachi High Technologies Corp.), and nitrogen adsorption isotherm measurements (BELSORP-mini, MicrotracBEL Corp.). The specific surface area of the samples were determined using the Brunauer-Emmet-Teller (BET) method. The total pore volume and specific surface area were calculated by the BET method, the mesopore volume by the Barrett-Joyner-Hallenda (BJH) method, and the micropore volume by the micropore analysis (MP) method. Thermogravimetric (TG) and differential thermal analysis (DTA) were recorded using a TG8221 (Rigaku Corp.) from room temperature to 800 °C in a flow of air and at a heating rate of 5 K min\(^{-1}\) using a platinum pan.

2.2. Preparation of STT-type Zeolite Membranes

The Si-STT zeolite was milled in a ball mill (UBM-S, Masuda Corp.) to reduce the particle size. A mixture of Si-STT zeolite and pure water was placed in a pot containing zirconium balls of 2 mm size. Then the mixture was milled at a rotation rate of 100 rpm for 8-48 h. The milled Si-STT zeolite seed crystals were used to coat the outside of a porous α-alumina support tube (outer diameter 16 mm, length 40 mm, pore size 0.5-1.0 μm, Hitachi Zosen Corp.). The tube was then calcined at 700 °C for 12 h, followed by immersion in a mixture of 1.0 $\text{SiO}_2 : 0.15-0.45 \text{TMAdaOH} : 24-54 \text{H}_2\text{O}$ (mole ratio) prepared by the same procedure as the seed crystals. Hydrothermal treatment was carried out at 150 °C for 6-10 days. Then, the tube was washed with a large volume of ion exchanged water and calcined at 500 °C for 10 h. The membranes were characterized by XRD and FE-SEM.

2.3. Gas Permeation Testing

Gas permeation experiments were performed using an apparatus constructed in our laboratory\(^{(15)}\). To measure the permeance for single gases, He, $\text{H}_2$, $\text{CO}_2$, $\text{CH}_4$, or $\text{SF}_6$ was fed to the outer (feed side) of the tube, and nitrogen (sweep gas) was fed to the inner (permeate side) of tube on the membrane side. The pressure difference between the feed and permeate sides was maintained at 100 kPa. The flow rates of the sweep gas and the gas permeating through the membrane were measured using bubble flow meters, and the gas concentrations were determined by gas chromatography (GC-8A, Shimadzu Corp.).

A gas separation test for an equimolar mixture of $\text{CO}_2/\text{CH}_4$ was conducted at 40 °C. The procedure was the same as for the single gas permeation tests. In addition, to confirm the effect of water on the gas permeation properties, a syringe pump was used to feed water to the feed side with the $\text{CO}_2/\text{CH}_4$ mixture. The water was evaporated by a ribbon heater looped around the tube.

3. Results and Discussion

3.1. Synthesis of Si-STT Zeolite

XRD patterns were recorded for samples prepared with hydrothermal synthesis of various durations (Fig. 1)\(^{(16)}\). The sample prepared with hydrothermal synthesis for 3 days showed an amorphous peak and no peaks assigned to STT-type zeolite. The sample prepared with hydrothermal synthesis for 3.5 days showed peaks consistent with STT-type zeolite. The peaks characterizing STT-type zeolite are very complex, so peaks derived from impurities may be obscured by the peaks of STT-type zeolite.

FE-SEM images were also recorded for the samples prepared with hydrothermal synthesis (Fig. 2). The sample prepared with hydrothermal synthesis for 3 days was amorphous (Fig. 2(a)). The sample prepared with hydrothermal synthesis for 3.5 days contained block-shaped crystals in layered sheets (Fig. 2(b)). The particle size was about 80 μm at 3.5 days (Fig. 2(c)), and increased to about 150 μm at 9 days (Fig. 2(d)). Therefore, STT-type zeolite formed between 3 days and 3.5 days, and crystal growth occurred after 3.5 days. Excessive synthesis time resulted in lower crystallinity and formation of amorphous material (Fig. 2(e)).

TG/DTA results for the sample prepared with hydrothermal synthesis for 5 days are shown in Fig. 3. Large mass losses were observed at around 100, 400,
and 600 °C. The loss at around 100 °C was attributed to desorption of adsorbed water, and losses at around 400 °C and 600 °C were presumably caused by decomposition of TMAdaOH. The weight loss at 400 °C was assigned to the decomposition and oxidation of TMA⁺ cations, and that at 500-700 °C was attributed to the decomposition and oxidation of pyrolysis products of TMA⁺ cations.

Based on the TG/DTA results, the effect of calcination temperature on nitrogen adsorption was investigated. Samples were calcined at 200, 500, or 700 °C, and the nitrogen adsorption isotherms were measured (Fig. 4). The sample calcined at 200 °C showed little adsorption. All calcined samples had IUPAC type I isotherms with features of microporous materials. The sample calcined at 500 °C showed greatly increased nitrogen adsorption, and the sample calcined at 700 °C showed a further slight increase in adsorption. The pore characteristics of STT-type zeolites calcined at different temperatures were evaluated (Table 1). The BET specific surface area increased with higher calcination temperature. The BET specific surface area of the sample calcined at 500 °C was 543 m² g⁻¹. Micropores accounted for most of the total volume in the calcined samples. Assuming that 100% of TMAdaOH was removed by calcination at 700 °C, then about 96% of TMAdaOH was...
was removed by calcination at 500 °C. Therefore, membrane calcination should be carried out at 500 °C to prevent crack formation because of thermal expansion at higher temperatures.

3.2. Synthesis of Si-STT Zeolite Membrane

The Si-STT particle size of about 100 μm was slightly too big for use as seed crystals, so particle size was reduced in a ball mill. The XRD patterns of the samples were recorded after milling (Fig. 5). Some changes in the peak ratios were observed as ball milling time increased, but the sample milled for 48 h retained the crystal structure of the STT-type zeolite. The FE-SEM images of the samples after ball milling are shown in Fig. 6. Some larger particles (diameter about 100 μm) remained in the mill after 8 h (Fig. 6(a)), but were not observed after milling for 24 h. In addition, the particle size of the sample obtained after milling for 48 h was relatively uniform and below 1 μm. Therefore, the sample was milled in a ball mill for 48 h before use as seed crystals to prepare the STT-type zeolite membranes.

XRD patterns were recorded of membranes prepared by hydrothermal synthesis for 6-10 days from gel with a mole ratio of 1.0 SiO2 : 0.25 TMAdaOH : 54 H2O, as shown in Fig. 7. All membranes showed peaks at 6° and 11°, which are attributed to STT-type zeolite. In addition, the peak intensity increased with longer hydrothermal synthesis time. FE-SEM images were recorded of the surfaces and cross-sections of membranes prepared with hydrothermal synthesis for 6, 8, or 10 days (Fig. 8). The surfaces of all membranes were covered by crystalline particles with relatively uniform particle sizes of about 2-3 μm. The particle shapes were similar regardless of the duration of hydrothermal synthesis. In addition, the membranes were all around 7-10 μm thick (Figs. 8(d)-8(f)).

The effect of the hydrothermal synthesis time on gas permeance was investigated (Fig. 9). Permeance of both H2 and CO2 increased with longer synthesis time, probably because of increased crystallinity of the membrane, as shown in the XRD patterns (Fig. 7). The peaks appearing at 2θ about 26° are related to the α-alumina support. In contrast, the lowest CH4 (0.38 nm) and SF6 (0.55 nm) permeances were obtained for the sample prepared with hydrothermal synthesis for 8 days. Therefore, formation of pinholes or cracks, which allowed for permeation of CH4 or SF6, decreased up to a hydrothermal synthesis time of 8 days, and increased with hydrothermal synthesis time of longer than 8 days. The permeation properties were related

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET specific surface area [m² g⁻¹]</th>
<th>Pore volume [cm³ g⁻¹]</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Total</td>
</tr>
<tr>
<td>as made</td>
<td>0.471</td>
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</tr>
<tr>
<td>200 °C</td>
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</tr>
<tr>
<td>500 °C</td>
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</tr>
<tr>
<td>700 °C</td>
<td>566</td>
<td>0.246</td>
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</table>

Fig. 5 XRD Patterns for STT-type Zeolites after Ball Milling for 8, 24, or 48 h

Fig. 6 Field Emission Scanning Electron Microscopy Images of STT-type Zeolites after Ball Milling for (a) 8 h, (b) Magnification of (a), (c) Ball Milling for 24 h, and (d) Ball Milling for 48 h
to the crystallinity, so CH₄ and SF₆ permeation should increase even with only a few pinholes or cracks. Therefore, CH₄ and SF₆ showed different permeation characteristics to H₂ and CO₂, which could permeate through the pores of the STT-type zeolite. Redissolution of the seed crystal was observed in the sample prepared with a synthesis time of 9 days (Fig. 2). Therefore, the STT-type zeolite layer might dissolve with excessive membrane synthesis time, and pinholes or cracks might form. Based on these experiments, 8 days was considered as the optimum membrane preparation time.

The XRD patterns of membranes prepared with different H₂O/SiO₂ ratios are shown in Fig. 10. Membranes prepared with H₂O/SiO₂ ratios between 34 and 54 showed peaks for STT-type zeolite. However, membrane prepared with a H₂O/SiO₂ ratio of 24 showed only small peaks at 6° and 11°, indicating that the sample had low crystallinity.

The effect of the H₂O/SiO₂ ratio in the synthesis gel on gas permeance was also investigated (Fig. 11). High gas permeance (10⁻⁷-10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹) was achieved for the membrane prepared with H₂O/SiO₂ = 24, and the permeance ratios were similar to the Knudsen diffusion ratios. Gas permeance decreased with higher ratio of H₂O/SiO₂ in the synthesis gel. The membrane prepared with H₂O/SiO₂ ratio of 54 had a
high permeance $H_2/SF_6$ ratio of 169. The STT-type zeolite membrane previously synthesized by Kida et al. showed $H_2/SF_6$ permeance ratio of 400 at 25 °C. The STT-type zeolite prepared in this study also showed high $H_2/SF_6$ permeance ratio at 40 °C. This result suggested that pinhole or crack formation was prevented by high water content in the synthesis gel. Slow growth of zeolite crystals is important to obtain a dense zeolite layer, and the optimal $H_2O/SiO_2$ ratio was 54 under the present conditions.

The effect of the SDA concentration in the synthesis gel on gas permeation was evaluated using XRD patterns of membranes prepared with different SDA/SiO$_2$ ratios (Fig. 12). All membranes showed peaks assigned to STT-type zeolite. The membrane prepared with SDA/H$_2$O of 0.15 had a relatively strong peak at 9°, suggesting that the membrane was orientated differently to the membranes prepared with other SDA/H$_2$O ratios. No large differences were observed in the XRD patterns of the membranes prepared with SDA/H$_2$O ratios between 0.25 and 0.45.

The gas permeances of membranes prepared with different SDA/SiO$_2$ ratios were measured (Fig. 13). Gas permeances were too big to measure accurately for the membrane with SDA/SiO$_2 = 0.15$ because the amount of SDA is too small to form a dense STT-type zeolite layer on the alumina support. Gas permeances
increased with higher SDA/SiO₂ ratio between 0.25 and 0.45. CH₄ and SF₆ permeances increased more with higher SDA/SiO₂ ratio compared with the H₂ and CO₂ permeances. The kinetic diameters of CH₄ and SF₆ are larger than the pore size of the STT-type zeolite, so increases in the CH₄ and SF₆ permeances indicate the formation of cracks or pinholes caused by the growth rate of the zeolite layer during the secondary growth process. High SDA content should induce a high growth rate, but a slow growth rate might be needed to obtain a dense STT-type zeolite layer because of the H₂O/SiO₂ ratio.

The effect of gas temperature on the gas permeances were investigated for a membrane prepared by hydrothermal synthesis for 8 days from synthetic gel with a mole ratio of 1.0 SiO₂ : 0.25 TMAdaOH : 54 H₂O. Permeation of small molecules through zeolite pores is known to occur via activated diffusion. The activation energies are obtained using the following equation:

\[ P = P_0 e^{-\frac{E_A}{RT}} \]

where \( P \) is the permeance [mol m⁻² s⁻¹ Pa⁻¹], \( P_0 \) is the pre-exponential factor [mol m⁻² s⁻¹ Pa⁻¹], \( E_A \) is the activation energy [J mol⁻¹], \( R \) is the gas constant [J mol⁻¹ K⁻¹], and \( T \) is the temperature [K]. The Arrhenius plots for the permeances of the STT-type zeolite membrane are shown in Fig. 14, and the \( P_0 \) and \( E_A \) of the gases are summarized in Table 2. H₂ and CH₄ permeances through amorphous silica membranes also involved activated diffusion. We previously reported the activation energies of H₂ and He permeating through silica membranes as 13-15 kJ mol⁻¹ and 8-10 kJ mol⁻¹, respectively\(^{18} \). In contrast, the gas permeances through the STT-type zeolite membrane showed low temperature dependency. Particularly, the SF₆ permeance showed no temperature dependency. The SF₆ molecule is larger than the pore size of STT-type zeolite, so must permeate through defects such as pinholes or cracks. CO₂ permeance showed a negative value. Permeance decreases with temperature in Knudsen diffusion. In addition, the adsorbed amount decreases with temperature. Therefore, the decrease in CO₂ permeance with temperature is caused by reduced adsorption of CO₂ or higher collision frequency between CO₂ molecules and pore walls. CO₂ permeance of chabazite-type zeolite membranes decreases with temperature\(^{20} \). Zeolites that contain aluminum have high polarity. Therefore, the amount of CO₂ molecules, which have a quadrupole moment, adsorbed on zeolites decreased with the temperature, so the CO₂ permeance also decreased. In contrast, STT-type zeolite membrane theoretically contains no aluminum. Therefore, the adsorbed CO₂ should have little effect on the CO₂ permeance.

The CO₂ and CH₄ permeances and permeance ratios were measured for single gases and a gas mixture (CO₂ : CH₄ of 1 : 1) at 40 °C (Table 3). CO₂ permeance for the gas mixture was higher than that for the single gas, and CH₄ permeance for the gas mixture was lower than that for the single gas. Adsorbed CO₂ induced higher CO₂ permeance and prevented permeation of other gases in the mixture, possibly caused by the different adsorption properties for each gas. The results for the gas

<table>
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<th>Table 2</th>
<th>Pre-exponential Factor Activation Energy of STT-type Zeolite Membrane</th>
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<tr>
<td></td>
<td>H₂</td>
</tr>
<tr>
<td>( P_0 ) [mol m⁻² s⁻¹ Pa⁻¹]</td>
<td>4.18 × 10⁻⁸</td>
</tr>
<tr>
<td>( E_A ) [kJ mol⁻¹]</td>
<td>3.53</td>
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<tr>
<th>Table 3</th>
<th>Permeances and Permeance Ratios under Different Feed Conditions</th>
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<tr>
<td></td>
<td>H₂O conc. [vol%]</td>
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<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Single gas</td>
<td>0</td>
</tr>
<tr>
<td>Mixed gas</td>
<td>0</td>
</tr>
<tr>
<td>Mixed gas</td>
<td>2.7</td>
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</table>

Fig. 14 Effect of the Feed Temperature on Permeance
mixture in the presence of water are also shown in Table 3. The saturated vapor pressure of H$_2$O is about 3.7 % (volume fraction). Both CO$_2$ and CH$_4$ permeances decreased in the presence of water. The permeance ratio was maintained at 16 despite the relatively high H$_2$O volume fraction of 2.7 %. CO$_2$ permeance of a FAU-type zeolite membrane containing aluminum in the presence of about 3 % (volume fraction) H$_2$O decreased to one-hundredth of that in dry conditions, and the membrane showed no selectivity for CO$_2$. Therefore, the STT-type zeolite membrane had almost the same permeance ratio regardless of the presence of H$_2$O because the STT-type zeolite theoretically contains no aluminum and should be hydrophobic.

4. Conclusions

STT-type zeolite was prepared by hydrothermal synthesis (> 3.5 days, 150 °C) from gel containing 1.0 SiO$_2$ : 0.50 TMAdaOH : 0.50 HF : 7.5 H$_2$O (mole ratio). Relatively uniform and small (> 1 μm) STT-type zeolite seed crystals were obtained by ball milling for 48 h, which maintained the STT-type zeolite crystal structure.

STT-type zeolite seed crystals were coated on an alumina porous support, and STT-type zeolite membrane was prepared by the secondary growth method. To obtain a dense STT-type zeolite membrane, the synthesis time and gel composition were optimized. The highest H$_2$/SF$_6$ permeance ratio (169) was obtained for the membrane prepared by hydrothermal synthesis for 8 days using synthetic gel with a mole ratio of 1.0 SiO$_2$ : 0.25 TMAdaOH : 54 H$_2$O. CO$_2$ permeance was higher and the CH$_4$ permeance was lower for a gas mixture compared to permeances for the single gases. In addition, although CO$_2$ permeance and permeance ratio decreased in the presence of water, the STT-type zeolite membrane showed selective permeance for CO$_2$.

References

要 旨

STT 型ゼオライト膜の調製と気体透過特性

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*2 日立造船（株）機能性材料事業推進室，551-0022 大阪市大正区船町1丁目2番11号

天然ガスの分離・精製プロセスにおけるゼオライト膜の利用が検討されている。天然ガス中には主成分である二酸化炭素やメタンのほかに硫化水素などの酸性ガスや水蒸気が存在する。従来のアルミニウムを含むゼオライト膜は、耐酸性や水蒸気存在下での透過流束の減少が生じるため、これらのプロセスへの適用が困難である。そのため、高い耐酸性および高い選択性を有するビュアシリカゼオライト膜が注目されている。そこで、本研究では比較的細孔容積が大きく、ビュアシリカの調製が報告されている STT 型ゼオライトに着目し、成膜条件について検討を行った。種結晶として用いる STT 型ゼオライト粒子の合成時およびポールミルによる粉砕時間の最適化を行った。8時間ポールミル処理した STT 型ゼオライト粒子をアルミナ多孔質支持体に担持し、2次成長法により STT 型ゼオライト膜を調製した。製膜時の合成時間の影響、構造規定剤（structure directing agent; SDA）および水濃度について検討を行った。1.0 SiO₂ : 0.25 TMAaOH : 54 H₂O のモル比で調整した溶液を用いて150℃、8日間熱処理した膜が最も高い水素と六フッ化硫黄の透過係数比169 を示した。