Synthesis and Characteristics of Al-containing ZSM-58 Zeolite Membrane for CO₂ Separation

E. Hayakawa and S. Himeno

Abstract—We prepared an Al-containing ZSM-58 zeolite membrane and compared it with the separation performance of an all-silica ZSM-58 zeolite membrane. First, the ZSM-58 zeolite crystals were synthesized from a solution with the same membrane synthesis solution composition, and the characteristics of ZSM-58 zeolite crystals with a difference in Si/Al molar ratio were studied. As-made crystals should have high porosity and crystallinity. All-silica and Al-containing ZSM-58 zeolite membranes were applied in the separation of an equimolar CO₂/CH₄ and CO₂/N₂ mixture of pressure drop and temperature. The Al-containing ZSM-58 zeolite membrane showed a higher selectivity than the all-silica ZSM-58 zeolite membrane, which was confirmed at a lower temperature and feed pressure.

Index Terms—CO₂ separation, DDR type zeolite, zeolite membrane, ZSM-58.

I. INTRODUCTION

Carbon dioxide is a cause of global warming, and CO₂ recovery technology for natural and flue gases is important in this regard. Among other separation technologies, a membrane separation method for CO₂ recovery can achieve higher energy and space savings and better economic characteristics. In particular, because the zeolite with an eight-membered oxygen ring (DDR, CHA, AEI, etc.) has pores close in molecular size to CO₂, N₂, and CH₄[1–14], it is a promising material for a CO₂ separation membrane.

DD3R zeolite has an all-silica DDR topology and has pores (0.36 × 0.44 nm) with an intermediate size between those of CO₂ molecules (0.33 nm) and CH₄ molecules (0.38 nm)[15]. Thus, many researchers have studied DD3R zeolite as a CO₂ separation membrane and reported a high CO₂/CH₄ separation performance [1], [4], [6], [16], [17]. By contrast, ZSM-58 zeolite has a DDR topology of Al-containing zeolite, which was reported to have a Si/Al molar ratio of 20 to ∞[18]. Al-containing zeolite has certain functions such as an ion exchange capacity and solid acid point.

Al-containing zeolite also has an increased CO₂ adsorption capability according to the decrease in Si/Al ratio [19], [20].

For example, adsorption CO₂/CH₄ selectivity of the LTA zeolite increased approximately 15 times if the Si/Al ratio of the LTA zeolite changed from ∞ to 2. Al-containing zeolite can be applied to pore size control using an ion exchange capacity such as from Na, K, Pb, and Pt [21], [22]. In addition, amine-modified zeolite has a high affinity for CO₂ [23].

Therefore, an Al-containing ZSM-58 zeolite membrane is expected to have a higher CO₂/CH₄ and CO₂/N₂ separation selectivity than DD3R, and an ion exchange and surface modification technology can be applied. However, it is difficult to prepare Al-containing zeolite membrane with high gas separation performance due to electrostatic repulsive force between silicate anion and negatively charged Al atom in zeolite framework [24], [25]. The synthesis of an all-silica ZSM-58 zeolite membrane was reported by Choi et al. [26]. However, there has been no reported synthesis of an Al-containing ZSM-58 zeolite membrane. In this study, we prepared an Al-containing ZSM-58 zeolite membrane, and investigated the separation characteristics of CO₂/CH₄ and CO₂/N₂ through a comparison with an all-silica ZSM-58 zeolite membrane.

II. EXPERIMENTAL

A. Materials and Chemicals

The following chemicals and materials were used in the resent work: Ludox HS-30 colloidal silica (30 wt%, Sigma-Aldrich), sodium hydroxide (97.0%, Wako), potassium hydroxide (97.0%, Wako), and sodium aluminate (Al/NaOH molar ratio = 0.77, Wako), terepine (98%, Combi-Blocks), iodomethane (99.5%, Wako), and ethanol (95%, Wako). In addition, CO₂ (99%), CH₄ (99%), and N₂ (99%) were used for the gas permeation tests.

Table I: Properties of Porous α-Alumina Tubular Support

<table>
<thead>
<tr>
<th>Outer diameter (mm)</th>
<th>Length (nm)</th>
<th>Porosity (%)</th>
<th>Pore diameter (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>100</td>
<td>30-50</td>
<td>Surface 0.2 Middle 0.9 Support 2-3</td>
</tr>
</tbody>
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Fig. 1. Cross-sectional SEM image of α-alumina tubular support used in this study.

The ZSM-58 zeolite membranes were prepared on the outside surface of porous α-alumina tubes (NGK Insulators, Ltd.). The porous α-alumina tubular supports used in this study are summarized in Table I. Fig. 1 shows a cross-section of scanning electron microscopy (SEM) image of a porous
α-alumina tubular support. This support consists of three layers, namely, the surface, middle, and support layers. Moreover, the pore diameter of the surface layer is 0.2 μm, and the length of the support is 30 or 100 mm. This support has a CO₂ permeance of 4 × 10⁻⁵ mol/s/m²/Pa at a feed pressure of 0.1 MPa. The CO₂ permeance of the DDR zeolite membrane is from 10⁻⁵ to 10⁻⁷ mol/s/m²/Pa, and the porous support has a sufficiently higher permeance than the zeolite layer.

B. Prepared ZSM-58 Seed Crystals and Seed Slurry

We prepared a ZSM-58 seed crystal by referencing a report by Valyocsik et al. [27]. Methyltropinium iodide (MTI) was used for the synthesis of the ZSM-58 zeolite as the structure directing agent (SDA). For the synthesis of MTI, 25.0 g of tropine was first dissolved in 100 g of ethanol. Next, 25.1 g of methyl iodide was then added to the solution, and the suspension was maintained under a reflux for 72 h. After cooling, the as-made MTI was washed with ethanol and dried at 343 K.

For the synthesis of the ZSM-58 crystals, a precursor solution with a composition molar ratio of MTI : NaOH : SiO₂ : H₂O = 0.25 : 0.33 : 1 : 40 was used. The precursor solution was prepared as follows: 6.4 g MTI was added to 42.9 g of H₂O (solution A), and 9.97 ml of a 3 M NaOH solution and 18.2 g of Ludox HS-30 were then added to solution A and stirred for 24 h (solution B). Solution B was then transferred into a Teflon-lined autoclave and maintained at 433 K for 72 h under rotation stirring. The as-synthesized ZSM-58 zeolite seed crystals were washed with DI water. After drying at 343 K overnight, ZSM-58 seed crystals were calcined at 973 K for 24 h at a ramp rate of 0.5 L min⁻¹. The calcined ZSM-58 zeolite particles were then milled, and the ball-milled particles were then dispersed in DI water, and ZSM-58 seed slurry with a particle size distribution of 0.2 μm was prepared using a centrifugation method. The ball-milled ZSM-58 seed particulates were coated onto the outermost surface layer of the alumina tubular support through a dip-coating method with this slurry. Fig. 2 shows an SEM image and X-ray diffraction (XRD) pattern of the ZSM-58 seed crystals in this work.

C. Synthesis of ZSM-58 Zeolite Crystals

We used the preparation method of a precursor solution as reported by Kumita et al. [28]. First, KOH and Ludox HS-30 were added to deionized water, and the solution was stirred for 20 min (solution A). The MTI, KOH, and deionized water were mixed in another container (solution B). If the Al-containing ZSM-58 zeolite was prepared, sodium aluminate was added into solution B. Solutions A and B were mixed and stirred for 24 h at 313 K. The samples of c1 and c2 had molar compositions of 0.1MTI : 0.1KOH : 1SiO₂ : 52H₂O and 0.05MTI : 0.05KOH : 1SiO₂ : 0.014Al₂O₃ : 52H₂O, respectively.

Next, 0.01 wt% of the ZSM-58 seed crystals were added to the precursor solution, and hydrothermal treatment was conducted at 413 K. The holding time of the hydrothermal treatment was two (c1) or five (c2) days. After hydrothermal treatment, the as-made crystals were washed with ethanol and deionized water and dried overnight at 343 K. The ZSM-58 zeolite crystals were calcined at 823 K for 4 h at a ramp rate of 0.5 L min⁻¹.

D. Synthesis of ZSM-58 Zeolite Membrane with Difference in Si/Al Molar Ratio

Ball-milled ZSM-58 seed particulates were coated onto the outermost surface layer of the alumina tubular support using a dip-coating method with ZSM-58 seed slurry. The ZSM-58 zeolite membranes were synthesized through a secondary growth method on the surface layer of the porous α-alumina tubular support. The precursor solution was prepared using a ZSM-58 zeolite crystal method (refer to Section 2.3), and all-silica (M1) and Al-containing ZSM-58 (M2) membranes were prepared using a gel composition of c1 and c2, respectively.

A α-alumina tubular support coated ZSM-58 seed crystal was placed vertically in a Teflon liner autoclave. A synthesis gel was then transferred into the Teflon liner autoclave and hydrothermal treatment was conducted at 413 K for two (M1) or five (M2) days. The autoclave was then cooled to room temperature, and the as-made membrane was washed with boiling water and dried at 343 K overnight. Different calcination methods were applied to M1 and M2 to inhibit the generation of cracks in the zeolite membrane.

An ozone de-template method was applied to M1 [16, 29], which was calcined at 473 K for 24 h under an ozone concentration of 120 g/Nm³ at a flow rate of 1 L/min.

A rapid thermal process (RTP) and a thermal calcination method were applied to M2 (Al-containing membrane) [17, 30]. M2 was then directly loaded into a preheated muffle furnace at 973 K for 1 min, withdrawn quickly, and cooled to room temperature. The ZSM-58 zeolite membrane was then calcined at 823 K for 4 h at a ramp rate of 0.5 L min⁻¹.

E. Characterization of ZSM-58 Zeolite Crystals and Membrane

The XRD (XRD-6100, Shimadzu) patterns were recorded using Cu Kα radiation. SEM images were obtained using a field-emission scanning electron microscope (JSM-6701, JEOL Ltd.) under an accelerating voltage of 1 kV and a work...
distance of 8–11 mm. The N₂ adsorption isotherms were measured using a BELSORP-Max (MicrotracBEL Co.) at 77 K. An elemental analysis of the ZSM-58 zeolite crystals was conducted using X-ray fluorescence (XRF, Rigaku ZSX Primus II, Rigaku Co.) analysis.

F. Gas Permeation and Separation Measurement

Single- and mixture-gas permeance tests using CO₂, CH₄, and N₂ were carried out on the ZSM-58 zeolite membranes. In this study, an equimolar mixture gas (CO₂/CH₄ and CO₂/N₂) was used to evaluate the permeance characteristics of the ZSM-58 zeolite membranes.

Single- and equimolar-mixture permeance tests as a function of the total feed pressure or temperature were also carried out on the ZSM-58 zeolite membranes. The total feed pressure was 0.3–0.9 MPa, and the permeate pressure was approximately 0.1013 MPa (atmospheric pressure). The gas permeation temperature was maintained at 273, 298, 348, 398, or 448 K. The gas flux and concentration were determined using a soap film flowmeter and gas chromatograph, respectively (490 Micro GC, GL Science).

The permeance, $P_i$ (mol/s/m²/Pa), was calculated using the following formula:

$$P_i = \frac{Q_i}{A \cdot \tau \cdot \Delta p_i}$$

where $Q_i$ (mol) is the mole of component $i$ permeated through the membrane for a time of $t$ (s), $A$ (m²) is the membrane area, and $\Delta p_i$ (Pa) is the differential partial pressure of component $i$ between the feed and permeate side.

The ideal selectivity is the ratio of the single-gas permeance. The separation selectivity is the ratio of the mixture-gas permeance. Therefore, the separation selectivity ($P_i / P_j$) for components $i$ over $j$ was calculated using the following formula:

$$\text{Selectivity} = \frac{P_i}{P_j}$$

Then, error rate of CO₂ permeance and CH₄ or N₂ permeance was approximately ±0.6 and ±7%, respectively. Moreover, the error rate of selectivity was approximately ±7%. The error rates were calculated from the standard deviation of the gas permeation time ($t$) and gas concentration.

III. RESULTS AND DISCUSSION

A. Research into Properties from N₂ Adsorption Isotherm of ZSM-58 Zeolite Crystals with Difference in Si/Al Molar Ratio

First, we investigated a N₂ adsorption isotherm of ZSM-58 zeolite crystal with a difference in Si/Al molar ratio. Here, c₁ and c₂ were prepared using a precursor solution with a Si/Al molar ratio of $\infty$ and 70, respectively. Based on XRF, c₂ was confirmed to have a Si/Al molar ratio of 81 in the crystals. Figs. 3 and 4 show an SEM image and XRD pattern of c₁ and c₂, respectively. The as-made crystals had a rhombohedral shape, which was confirmed using a DD3R crystal reported in a previous study, and confirmed a high crystallinity through the XRD pattern.

Figs. 5 and 6 respectively show N₂ adsorption isotherm and the FT-IR spectrum of as-made ZSM-58 zeolite crystals. Table II shows the characteristics of the ZSM-58 zeolite crystals based on the measured N₂ adsorption isotherm.

The as-made crystals had a type I adsorption isotherm, which is obtained in microporous materials [31]. The ZSM-58 zeolite showed a BET surface area of from 300 to 400 m²/g, which is consistent with the previous reports.
surface area was reported by Kuhn et al. [32] because the template removal is difficult for zeolites with a low Si/Al ratio [33].

Meanwhile, FT-IR spectrums of zeolite crystals showed conformed peaks of C-H bonds of MTI molecules assigned from 2,800 to 3,000 and from 1,400 to 1,500 cm$^{-1}$. Therefore, MTI molecules in ZSM-58 zeolite pores were able to be removed through thermal calcination at 823 K.

**B. Characterization of ZSM-58 Zeolite Membrane**

Fig. 7 shows XRD pattern of a ZSM-58 membrane, which suggests that M1 and M2 have a high purity ZSM-58 zeolite layer. As shown in Figs. 8 and 9, M1 is covered with approximately 1 μm of ZSM-58 polycrystalline grains, and the membrane thickness, including the composition layer, is approximately 5 μm. In contrast, M2 showed a larger polycrystalline grain and thicker membrane thickness than M1.

![Fig. 7. XRD patterns of M1 and M2. The triangles (▼) indicate the α-alumina peak.](image)

![Fig. 8. SEM images of membrane surface of M1 and M2.](image)

![Fig. 9. SEM images of cross-section of M1 and M2.](image)
C. Effect of Pressure Drop at CO\textsubscript{2}/CH\textsubscript{4} Condition

Fig. 10 shows the pressure dependence of single and mixture permeance (single $P_{CO_2}$ and $P_{CH_4}$, and mixed $P_{CO_2}$ and $P_{CH_4}$) through all-silica (M1) and Al-containing ZSM-58 zeolite membranes (M2). M1 showed a mixed $P_{CO_2}$ of $17 \times 10^{-8}$ mol/s/m\textsuperscript{2}/Pa and single $P_{CO_2}$ of $26 \times 10^{-8}$ mol/s/m\textsuperscript{2}/Pa, whereas M2 had a $P_{CO_2}$ mixture of $6.3 \times 10^{-8}$ mol/s/m\textsuperscript{2}/Pa and single $P_{CO_2}$ of $9.1 \times 10^{-8}$ mol/s/m\textsuperscript{2}/Pa at a pressure decrease of 0.2 MPa. Because M2 has a dense and thick zeolite layer, it shows a $P_{CO_2}$ of approximately 40% of M1.

The single and mixed $P_{CO_2}$ decreased with an increase in pressure drop because the adsorption of CO\textsubscript{2} molecules in the zeolite pores became saturated at a high-pressure region.

The value of $P_{CH_4}$ for M1 increased as the pressure drop increased, whereas that for M2 was independent of the pressure drop. This difference is speculated to be due to the amount of large crystal grains.

The M2 was calcined through RTP and the thermal calcination method. It is thought that the rapid thermal treatment caused a bonding surface silanol of the zeolite crystal and inhibited the cracks and large crystal grains [17]. However, because there is no effect of RTP treatment owing to few surface silanol groups in the all-silica zeolite membrane, ozone de-template method was applied to M2. As a result, M2 shows an extremely low $P_{CO_2}/P_{CH_4}$, and a very high $P_{CO_2}/P_{CH_4}$, as shown in Fig. 11.

D. Effects of Temperature at CO\textsubscript{2}/CH\textsubscript{4} Condition

Fig. 12 and 13 shows the pressure dependence of single gas and mixture permeance and CO\textsubscript{2}/CH\textsubscript{4} selectivity through M1 and M2. M1 showed a $P_{CO_2}$ mixture of $21 \times 10^{-8}$ mol/s/m\textsuperscript{2}/Pa and single $P_{CO_2}$ of $31 \times 10^{-8}$ mol/s/m\textsuperscript{2}/Pa, whereas M2 showed a $P_{CO_2}$ mixture of $14 \times 10^{-8}$ mol/s/m\textsuperscript{2}/Pa and single $P_{CO_2}$ of $16 \times 10^{-8}$ mol/s/m\textsuperscript{2}/Pa at a temperature of 273 K.

The single and mixed $P_{CO_2}$ increased with an increase in temperature because the adsorption of CO\textsubscript{2} molecules in the zeolite pores began to become lower at a low-temperature region.

Fig. 11. $P_{CO_2}/P_{CH_4}$ of single-gas and equimolar CO\textsubscript{2}/CH\textsubscript{4} mixture of pressure drop at 298 K, and permeated side of atmospheric pressure for M1 and M2. Open symbols (○, □) correspond to single-gas selectivity of CO\textsubscript{2} and CH\textsubscript{4}, and closed symbols (●, ■) correspond to the mixture permeance of CO\textsubscript{2} and CH\textsubscript{4}.

Fig. 12. Permeance of single gas and equimolar CO\textsubscript{2}/CH\textsubscript{4} mixture with temperature at a pressure drop of 0.2 MPa and permeated side of atmospheric pressure for M1 and M2. Open symbols (○, □) correspond to the single-gas permeance of CO\textsubscript{2} and CH\textsubscript{4}, and closed symbols (●, ■) correspond to the mixed permeance of CO\textsubscript{2} and CH\textsubscript{4}.
Because the CO$_2$ adsorption coverage decreased as the temperature increased, the single and mixed CO$_2$ decreased according to the increased separation temperature. The CO$_2$ and CO$_2$/CH$_4$ of M2 were significantly high at 273 K. Al-containing zeolite strongly adsorbs CO$_2$ molecules in low temperature. Therefore, M2 (single, 1,500; mixed, 1,200) has a higher CO$_2$/CH$_4$ (single, 350; mixture, 300) than M1 at 273 K. In contrast, CO$_2$/CH$_4$ of M2 (single, 240; mixture, 140) is close to CO$_2$/CH$_4$ of M1 (single, 81; mixture, 71) at 448 K because the CO$_2$ adsorption coverage is low in a high-temperature region.

E. Effects of Pressure Drop at CO$_2$/N$_2$ Condition

Figs. 14 and 15 show the pressure dependence of the permeance (single CO$_2$ and N$_2$; mixed CO$_2$ and N$_2$) and CO$_2$/N$_2$ selectivity (single CO$_2$/N$_2$; and mixed CO$_2$/N$_2$) through M1 and M2, respectively. M1 showed a CO$_2$ mixture of $28 \times 10^{-8}$ mol/s/m$^2$/Pa and CO$_2$/N$_2$ mixture of 44, whereas M2 showed a CO$_2$ mixture of $12 \times 10^{-8}$ mol/s/m$^2$/Pa and CO$_2$/N$_2$ mixture of 53 of at a pressure drop of 0.2 MPa. As with the CO$_2$/CH$_4$ separation, CO$_2$ decreased as the pressure drop increased.

The single and mixed N$_2$ were independent of the pressure drop, and the mixed N$_2$ was higher than the single N$_2$ for both membranes. Here, N$_2$ was over 10-times that of CH$_4$, which suggests that N$_2$ molecules diffused faster into zeolite pores than CH$_4$ molecules. Therefore, the CO$_2$/N$_2$ adsorption selectivity was important for CO$_2$/N$_2$ separation. N$_2$ permeation was inhibited owing to strongly adsorbed CO$_2$ molecules in the zeolite pore in the mixed system [16], [17].

The single CO$_2$/N$_2$ of both membranes was in the range of 18–30, and a large difference was not confirmed. When the pressure drop was changed from 0.2 to 0.8 MPa, the mixture CO$_2$/N$_2$ of M1 and M2 decreased from 44 to 30 and 53 to 45, respectively. Because zeolite with a low Si/Al molar ratio has a high CO$_2$ adsorption capacity [19], [20], we considered that M2 showed a higher CO$_2$/N$_2$ than M1.
F. Effects of Temperature at CO\textsubscript{2}/N\textsubscript{2} Condition

Figs. 16 and 17 show the temperature dependence of permeance and CO\textsubscript{2}/N\textsubscript{2} selectivity through M1 and M2, respectively. M1 showed a CO\textsubscript{2} mixture of 34 × 10\textsuperscript{-8} mol/s/m\textsuperscript{2}/Pa and PCO\textsubscript{2}/PN\textsubscript{2} mixture of 57, whereas M2 showed CO\textsubscript{2} mixture of 17 × 10\textsuperscript{-8} mol/s/m\textsuperscript{2}/Pa and PCO\textsubscript{2}/PN\textsubscript{2} mixture of 64 at a temperature of 273 K.

Here, PCO\textsubscript{2} and PN\textsubscript{2} decreased as the temperature increased because the adsorption coverage decreased at a high temperature. Although the PCO\textsubscript{2} and PCO\textsubscript{2}/PN\textsubscript{2} mixture was higher than a single system at less than 350 K, the magnitude of the correlation of PCO\textsubscript{2} and PCO\textsubscript{2}/PN\textsubscript{2} between the mixed and single gases was reversed at over 350 K. Moreover, mixture PN\textsubscript{2} was similar than single system at over 350 K. Their trend was caused by a suppression of the N\textsubscript{2} permeation owing to a high CO\textsubscript{2} adsorption coverage at low temperature (< 350 K).

However, CO\textsubscript{2} permeation was inhibited the adsorption competition between N\textsubscript{2} and CO\textsubscript{2} owing to the decrease in CO\textsubscript{2} adsorption coverage at high temperature, and the mixed PCO\textsubscript{2} was lower than the single PCO\textsubscript{2}. Therefore, PCO\textsubscript{2} and PCO\textsubscript{2}/PN\textsubscript{2} mixtures were close to the single PCO\textsubscript{2} and PCO\textsubscript{2}/PN\textsubscript{2}. M2 showed a higher PCO\textsubscript{2}/PN\textsubscript{2} mixture (64) than M1 (57) at 273 K owing to the difference in CO\textsubscript{2} adsorption capacity, and M2 showed a similar PCO\textsubscript{2}/PN\textsubscript{2} mixture (11) than M1 (13) at 448 K.

IV. CONCLUSION

We successfully synthesized an Al-containing ZSM-58 zeolite membrane on an α-alumina tubular support, which was compared with an all-silica ZSM-58 zeolite membrane. The Al-containing ZSM-58 zeolite membrane could suppress the occurrence of cracks under high-temperature calcination using RTP treatment. The Al-containing ZSM-58 zeolite membrane showed higher separation selectivity than the all-silica ZSM-58 zeolite membrane, and exhibited a CO\textsubscript{2}/CH\textsubscript{4} selectivity of 540 and CO\textsubscript{2}/N\textsubscript{2} selectivity of 53 at 298 K, and a feed pressure of 0.3 MPa. The ZSM-58 zeolite membrane with high Al concentration is necessary to achieve high separation performance. Although ZSM-58 membrane with Si/Al of 70 could be prepared in this study, the ZSM-58 zeolite crystal can consist of Al to Si/Al of 20. The low Si/Al ZSM-58 zeolite membrane is expected to achieve a high CO\textsubscript{2} separation performance through a surface modification technology such as an amine-modified surface.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

Eiji Hayakawa conducted experiment and research under the guidance of Shuji Himeno, and this paper was written jointly Eiji Hayakawa and Shuji Himeno.

ACKNOWLEDGMENT

This work was supported by JSPS KAKENHI Grant (Number 15K12227). The X-Ray fluorescence analysis was performed at the Nagaoka University of Technology Analysis and Instrumentation Center.

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