1. Introduction

The separation of a propylene/propane mixture into its constituents by distillation is recognized as one of the most energy-consuming processes in the petrochemical industry. Membrane separation processes are attractive alternatives to distillation as they have the potential to significantly reduce energy consumption. Recently, zeolitic imidazolate framework-8 (ZIF-8) has gained focus as one of the most promising membrane materials for propylene/propane separation. ZIF-8 is composed of zinc atoms with 2-methylimidazole as a ligand; this combination forms a sodalite zeolite structure with large cavities connected through a small pore aperture. Zhang et al. reported that the effective aperture size of ZIF-8 for molecular sieve application was between 0.40 nm and 0.42 nm, which corresponds to the van der Waals diameter of propylene and propane, respectively. Consequently, ZIF-8 has gained recognition as a promising material for the separation of propylene/propane based on the difference in the molecular size of these two species. ZIF-8 membranes are conventionally prepared by the in-situ growth method, secondary growth method, and the counter diffusion method. Pan et al. first reported the effective separation of propylene/propane with ZIF-8 membranes using the secondary growth method, achieving a selectivity of up to 50 for an equimolar mixture of propylene/propane. Subsequently, Kwon and Jeong and Liu et al. also reported ZIF-8 membranes with a comparable propylene/propane separation performance. Recently, the counter diffusion approach, which allows for preparation of ZIF-8 selective layers with fewer defects via a simple protocol, has gained prominence.
the interface of the two corresponding solutions, and crystallization occurs until the entire path through the ZIF-8 layer becomes “plugged.” Kwon and Jeong also reported the preparation and permeation properties of ZIF-8 membranes using the counter diffusion method, where a selectivity of up to 55 was achieved for an equimolar mixture of propylene/propane19). We have recently reported the preparation of ZIF-8 membranes with a propylene/propane ideal separation factor of 59, for which the ZIF-8 layer was prepared within the pores of an α-alumina porous substrate using the counter diffusion method21), subsequent to the development of the HKUST-1 membrane using the counter diffusion method23). Brown et al. recently reported the scalable preparation of ZIF-8 membranes, where the ZIF-8 layer was formed on the inner surface of polymeric hollow fibers using interfacial microfluidic membrane processing (IMMP) based on the counter diffusion concept20), giving rise to a propylene/propane selectivity as high as 12.

In the counter diffusion method, the rates of reaction and diffusion strongly impact the structure and permeation properties of the resultant ZIF-8 membranes. A thinner selective layer with enhanced permeation is generally formed when the reaction rate is higher and the diffusion rate is lower at the interface of the two solutions19). We recently reduced the thickness of ZIF-8 membranes by increasing the zinc nitrate concentration in the inner part of the capillary substrate, which was derived from the enhanced reaction rate due to the higher solution concentration24). Furthermore, we reported the effect of the solution interface by using an immiscible solution pair, as well as the effect of the solution concentration on the structure and permeation properties of ZIF-8 membranes25,26). In addition to the preparation conditions, the reaction temperature is also expected to exert a significant influence on the rate of reaction and diffusion in the counter diffusion method; however, this effect has not yet been reported.

In the present study, we examine the effect of the reaction temperature on the structure and single-component and binary gas permeation properties of ZIF-8 membranes prepared by the counter diffusion method. A higher reaction temperature is expected to facilitate both the reaction of ZIF-8 formation and the interdiffusion of the solutes. Therefore, the effect of the reaction temperature on the membrane structure and gas permeation properties should be examined by considering these complicated factors. For this purpose, we used dimethylformamide (boiling point: 153 °C) as a solvent in the preparation of ZIF-8 membranes in order to control the reaction temperature within the wide range of 25-125 °C. The substrate was then placed under vacuum at 0.01 MPa for approximately 60 s in order to remove any bubbles from the pores of the substrate. A plastic plug was inserted into the open top end of the substrate in order to seal the inner part. The substrates soaked in respective zinc nitrate solutions were heated at the specified reaction temperatures. The entire substrate was then immersed in 0.8 M 2-methylimidazole solution in N,N-dimethylformamide preheated at the specified reaction tempera-

2. Experimental

2.1. Membrane Preparation

A porous α-alumina hollow capillary substrate with a diameter of 3 mm, an average pore diameter of 150 nm, a porosity of 46 %, and a thickness of 350 μm was obtained from NOK Corp. The substrate was cut into pieces of 45 mm length, washed with acetone, and then dried under vacuum. Methanol, N,N-dimethylformamide, and zinc nitrate hexahydrate were purchased from Wako Pure Chemical Industries, Ltd.; 2-methylimidazole was purchased from Sigma-Aldrich Co., LLC and used as received. ZIF-8 membranes were prepared by the counter diffusion method, as shown in Fig. 1. The reaction temperature was varied as 25, 50, 75, 100, and 125 °C for ZIF-8 membranes M1, M2, M3, M4, and M5, respectively. One end of the substrate was sealed with molten glass to separate the inner and outer regions. The substrate was then completely immersed in 0.4 M (1 M = 1 mol L⁻¹) zinc nitrate solution in N,N-dimethylformamide in a glass vial. The glass vial was then placed under vacuum at 0.01 MPa for approximately 60 s in order to remove any bubbles from the pores of the substrate. A plastic plug was inserted into the open top end of the substrate in order to seal the inner part. The substrates soaked in respective zinc nitrate solutions were heated at the specified reaction temperatures. The entire substrate was then immersed in 0.8 M 2-methylimidazole solution in N,N-dimethylformamide preheated at the specified reaction tempera-

![Fig. 1 Schematic Illustration of the Counter Diffusion Method Used in this Study](image-url)
ture. The glass vial was sealed and maintained at the specified reaction temperature for 72 h. The glass vial was allowed to cool to room temperature, and the obtained ZIF-8 membranes were washed with methanol at 50 °C for 24 h and dried at 90 °C for 24 h in a vacuum oven.

The prepared ZIF-8 membranes were gravimetrically characterized based on the loading capacity (%) using Eq. (1):

\[ \text{Loading capacity} = 100 \times \frac{w_m - w_s}{w_s} \]  

(1)

where \( w_m \) (g) is the weight of the ZIF-8 membrane, and \( w_s \) (g) is the weight of the substrate.

2.2. Analysis

The crystal structures of the ZIF-8 membranes were determined by XRD analysis with Cu-K\( \alpha \) radiation, using a Bruker D8 Advance instrument. The membranes were divided into small pieces and placed on a plastic cell for measurement. The diffraction patterns were acquired at room temperature in the 2\( \theta \) range 5-40°. The crystallite growth of ZIF-8 was determined from the intensity ratio (%) of the X-ray diffraction (XRD) patterns using Eq. (2):

\[ \text{Intensity ratio} = 100 \times \frac{I_{011}}{I_{sub}} \]  

(2)

where \( I_{011} \) is the intensity of the 011 reflection of ZIF-8, and \( I_{sub} \) is the intensity of the 104 reflection of the substrate.

The surface and cross-sectional structures of the ZIF-8 membranes were analyzed via scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) analysis using an S-3400N instrument (Hitachi High-Technologies Corp.).

2.3. Gas Permeation Measurements

The single-component gas permeation properties were determined using a high-vacuum time-lag method under a pressure difference of 0.1 MPa for propylene and propane. Before the permeation analyses, the membranes were vacuum-dried at 90 °C for more than 12 h to remove any residual water and gas molecules. Both the feed and permeate sides of the membranes were evacuated prior to each analysis. The gas permeances are expressed in SI units as mol m\(^{-2}\) s\(^{-1}\) Pa\(^{-1}\). The ideal separation factor of propylene/propane is defined as the ratio of the permeance of propylene to propane.

The binary component gas permeation properties of the membrane for the propylene/propane mixtures were assessed using a time-lag method with the shell side feed configuration. The feed pressure was controlled by adjusting the back pressure regulator from 0.1 to 0.7 MPa on the retentate line, and the permeate side was evacuated by using a rotary vacuum pump. The total feed flow rate was fixed at 200 mL min\(^{-1}\), and the feed composition was controlled by mass flow controllers located in each line for propylene and propane.

The gas compositions of the feed, permeate, and retentate streams were determined on-line through the sampling rotary valve using gas chromatography.

3. Results and Discussion

3.1. Synthesis of ZIF-8 Membranes

ZIF-8 membranes with different internal and cross-sectional structures were prepared by the counter diffusion method by varying the reaction temperature from 25 to 125 °C using a fixed concentration of the reaction solutions. Figure 2 a) shows the XRD pattern of the substrate, and Fig. 2 b) shows the XRD pattern of the ZIF-8 crystals, simulated from the crystallographic data. The XRD patterns for M1-M5 show peaks corresponding to the substrate as well as ZIF-8, which confirms the presence of ZIF-8 in the resultant membranes (Fig. 2 c)-g)). Figure 3 shows the loading capacity and intensity ratio of the ZIF-8 membranes. The loading capacity and intensity ratio concurrently increased on increasing the reaction temperature from 25 to 75 °C. Both the loading capacity and the intensity ratio achieved maximum values at 75 °C, and then concurrently decreased on further increasing the reaction temperature from 75 to 125 °C.

The SEM images of the outer- and inner-membrane surfaces, as well as the cross-sectional SEM images of the membranes and magnified SEM images of the outermost section of the membranes, along with the EDX line analysis. The outer surface of the membranes were observed to be lightly covered with small ZIF-8 particles with diameters of less than 1 μm for all membrane
samples (Fig. 4(a)); the observed structure on the outer membrane surfaces is similar to those observed in our previous studies. In the case of M1, M2, and M3, a small amount of ZIF-8 particles of up to 3 μm in diameter were observed on the inner-membrane surfaces (Fig. 4(b)). In the case of M4 and M5, no ZIF-8 particles were observed on the inner surface, and the substrate remained exposed as shown in Fig. 4(b), which is also similar to our previous observations.

The characteristic properties of the ZIF-8 membranes, such as the loading capacities, intensity ratio, and outer- and inner-surface structures can be explained in combination with the cross-sectional SEM-EDX analyses, as shown in Fig. 4(c). The ZIF-8 membrane M1 shows the presence of a ZIF-8 layer in which the outermost section of the substrate is about 70 μm thick. However, the distribution of the ZIF-8 layer is relatively broad in the inner part of the substrate, and ZIF-8 particles were also formed on the inner surface of the substrate. The formation of ZIF-8 particles on the inner surface of the substrate is due to the interdiffusion of zinc nitrate and 2-methylimidazole solutes owing to the lower reaction rate at the low reaction temperature of 25 °C. The thickness of the ZIF-8 layer formed in the outermost section of the substrate decreased with increasing reaction temperature; ZIF-8 layers with respective thicknesses of about 50 μm and 40 μm were formed for M2 and M3. The loading capacity as well as the intensity ratio increased with increasing reaction temperature, and the cross-sectional analyses showed a thinner and more definite layer structure of ZIF-8 species for M2 and M3 than that of M1. This is probably due to the increase in the reaction rate as the reaction temperature increased.
temperatures. The loading capacity decreased on increasing the reaction temperature from 75 to 125 °C, which also indicates the definite layer structure of ZIF-8 species at the outermost section of the substrate. Thus, it is clear that well-defined ZIF-8 layers were formed in the outermost section of the substrate at higher reaction temperatures. The rate of reaction is higher than the rate of diffusion at the higher reaction temperatures used in this study.

3.2. Single-component and Binary Gas Permeation Properties

The single-component gas permeation properties of the membranes were measured using propylene and propane with a pressure difference of 0.1 MPa at 25 °C (Fig. 5). The respective propylene permeances of M1 and M2 were 7.0 × 10⁻⁹ and 8.0 × 10⁻⁹ mol m⁻² s⁻¹ Pa⁻¹. Propylene permeance decreased for membranes prepared at higher reaction temperatures, and dropped to 3.7 × 10⁻⁹ mol m⁻² s⁻¹ Pa⁻¹ for both M3 and M4. The propylene permeance of M5 was slightly higher at 5.7 × 10⁻⁹ mol m⁻² s⁻¹ Pa⁻¹. The ideal separation factor for propylene/propane was 2.7 for both M1 and M2. The ideal separation factor increased to 7.9 and 12.8 for M3 and M4, respectively. The ideal separation factor eventually dropped to 5.3 for M5 prepared at the highest reaction temperature of 125 °C. We previously reported an ideal separation factor for propylene/propane of over 50 for ZIF-8 membranes prepared from methanolic solution. However, the highest ideal separation factor for propylene/propane in this study is lower than that of our previous studies, which may arise from the difference in the solvent used in the synthesis. The extent of membrane solvation in dimethylformamide (an aprotic polar solvent) used in this study is not as high as that in methanol (a protic polar solvent) used in our previous studies. Therefore, it is possible that the rate of reaction is lower in this study where DMF is used as a solvent than in our previous studies using methanol. In this case, the size of the ZIF-8 crystals may be reduced and the degree of crystallinity may be lowered, which are less favorable situations for the preparation of a well-defined ZIF-8 selective layer with a high ideal separation factor for propylene/propane. However, analysis of the precise structure of the ZIF-8 selective layer is difficult at this point due to the limited amount of ZIF-8 formed within the pore of the substrate.

In the case of M1 and M2, the rate of reaction should be low due to the lower reaction temperature. Small defects in the ZIF-8 layer were not effectively removed; therefore, the ideal separation factor remained low. The rate of reaction should increase on increasing the reaction temperatures for M3 and M4, and the defects in the ZIF-8 selective layer were effectively removed. As a result, a maximum ideal separation factor of 12.8 was obtained for M4 prepared at 100 °C. In the case of M5 prepared at 125 °C, a higher propylene permeance was obtained; however, in an opposing trend, the ideal separation factor for propylene/propane decreased. The rate of reaction for M5 should be high at the high reaction temperature; therefore, the polycrystalline structure may be different from that of the ZIF-8 membranes prepared at low reaction temperatures. The crystalline selective ZIF-8 layer in M5 may contain more intercrystalline gaps and twinning defects, which would decrease the ideal separation factor for propylene/propane. Thus, the reaction temperature exerts significant influence on the single-component gas permeation properties of the ZIF-8 membranes. The ensuing detailed discussions of the propylene/propane separation properties focus on M4, which has the highest ideal separation factor for propylene/propane.

3.3. Separation of Propylene/propane Mixture

Figure 6(a) shows the effect of propylene fraction in the feed on the permeance and selectivity of M4 for propylene and propane under a total pressure difference of 0.1 MPa at 25 °C. The permeance of propylene decreased slightly from 1.4 × 10⁻⁹ to 1.1 ×
10⁻⁹ mol m⁻² s⁻¹ Pa⁻¹ as the propylene fraction in the feed increased from 0.1 to 0.9. The decrease in the propylene permeance with increasing partial pressure can be explained in terms of Langmuir-type adsorption based on the equilibrium isotherm, as discussed previously22,29. The permeance of propane decreased slightly from 2.1 × 10⁻¹⁰ to 1.5 × 10⁻¹⁰ mol m⁻² s⁻¹ Pa⁻¹ on increasing the propylene fraction in the feed. Thus, the propylene/propane selectivity of M₄ was almost constant around 7. The propylene permeance and propylene/propane selectivity determined in the binary component gas permeation measurements were lower than those obtained from the single-component measurements. This is probably due to the inhibition of propylene permeation by the coexistence of propane.

Figure 6(b) shows the effect of the total feed pressure (from 0.1 to 0.7 MPa) on the permeance and selectivity of M₄ for propylene and propane using an equimolar mixture of propylene and propane at 25 °C. The propylene permeance decreased slightly from 1.2 × 10⁻⁹ to 1.0 × 10⁻⁹ mol m⁻² s⁻¹ Pa⁻¹ with an increase in the total feed pressure due to the Langmuir-type adsorption as discussed earlier. The propane permeance increased from 1.7 × 10⁻¹⁰ to 2.0 × 10⁻¹⁰ mol m⁻² s⁻¹ Pa⁻¹ on increasing the total feed pressure which can be explained by the increase of the viscous flow through the small defect remaining in the ZIF-8 selective layer. The decrease in the propylene permeation at higher total feed pressures is consistent with the observations from the previous study18. The resultant propylene/propane selectivity decreased slightly from 6.9 to 5.0 with an increase in the total feed pressure.

Figure 7 shows the effect of declining permeation temperature (100-0 °C) on the permeance and selectivity of M₄ for propylene and propane using an equimolar mixture of propylene and propane. The propylene permeance decreased slightly from 2.2 × 10⁻⁹ to 1.8 × 10⁻⁹ mol m⁻² s⁻¹ Pa⁻¹ as the permeation temperature decreased. The propane permeance also decreased from 2.3 × 10⁻¹⁰ to 1.9 × 10⁻¹⁰ mol m⁻² s⁻¹ Pa⁻¹ with decreasing permeation temperature, and the resultant propylene/propane selectivity was almost constant around 10.

Permeation of propylene and propane with ZIF-8 membrane is governed by solution-diffusion mechanism. The analysis of partial and total feed pressure affected the sorption step as shown in Figs. 6(a) and 6(b), whereas the analysis of the temperature affected both sorption and diffusion step. The permeation of propylene and propane showed the activated diffusion from the temperature analysis as shown in Fig. 7. Therefore, it is concluded that the permeation of propylene and propane is governed by molecular sieve mechanism for ZIF-8 membrane prepared in this study.

The microstructure of ZIF-8 membrane prepared in this study can be different from those in the previous studies due to the unique preparation method of counter diffusion which can decrease the defect in the ZIF-8 selective layer. In the previous report, the propylene permeance and propylene/propane selectivity were found to increase with decreasing temperature due to increased adsorption of these species in the lower temperature range22. The trend obtained in this study is opposite to that of the previous report, which may be attributed to microstructural differences in the selective ZIF-8 layer. The size of the particles in the ZIF-8 layer prepared herein within the pore of the porous substrate is at least smaller than the pore sizes of 150 nm, which is smaller than those of the previous reports. This may lead to different adsorption properties from that documented in other reports. However, it is difficult to analyze the complexity of the structure at this point due
to the small amount of ZIF-8 formed in the membrane.

4. Conclusion

In conclusion, the effects of the reaction temperature on the structure and single-component and binary gas permeation properties of ZIF-8 membranes were assessed. ZIF-8 membranes were prepared by the counter diffusion method using dimethylformamide as a solvent in order to control the reaction temperature to 25-125 °C. The thickness of the ZIF-8 layer formed in the outermost section of the resultant ZIF-8 membranes decreased from 70 to 40 μm and the layer was also characterized by a definite layer structure with increasing reaction temperature. The rate of reaction exceeds the rate of diffusion at higher reaction temperatures. A propylene permeance of $2.2 \times 10^{-9}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ (with a propylene/propane selectivity of around 10) was obtained in the binary gas permeation assessment of the ZIF-8 membrane prepared at 100 °C, and activated diffusion of propylene permeation was observed from the permeation temperature-dependence analysis. It was clarified that the reaction temperature used in the preparation of the ZIF-8 membranes using the counter diffusion method has a significant impact on the structure and gas permeation properties of the resulting membranes. Further studies are underway to improve the propylene/propane selectivity with ZIF-8 membranes based on the current findings such as solution concentration and reaction temperature in the counter diffusion method.

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References

要 旨
対向拡散法によるプロピレン／プロパン分離用 ZIF-8膜の作製における反応温度の影響

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金属有機構造体の一種である zeolitic imidazolate framework-8 (ZIF-8) は、プロピレン／プロパン分離用の新規膜素材として注目される。ZIF-8膜の作製方法として、直接重合法、二次成長法、および対向拡散法が報告されている。特に対向拡散法は、分離層における欠陥を大幅に低減できることが特長である。本研究では、対向拡散法を用いた ZIF-8膜の作製において、反応温度が ZIF-8膜の構造とプロピレンとプロパンの透過特性に与える影響を検討した。α-アルミナ多孔質中空管を支持体として用いて、反応温度25～125℃の範囲において対向拡散法による ZIF-8膜の作製を行った。反応温度25℃において得られた ZIF-8膜は、ZIF-8層厚さが70μmであったが、反応温度125℃においては ZIF-8層厚さが40μmに減少した。反応温度100℃において、プロピレン透過度2.2×10⁻⁷mol m⁻²s⁻¹Pa⁻¹、プロピレン／プロパン理想分離係数10が得られた。各反応温度において得られた ZIF-8膜の構造の解析と、単成分および混合成分のプロピレンとプロパンの透過特性の解析を行った。

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