Synthesis and Gas Permeation Properties of AEI Zeolite Membranes by DIPEA as a Template

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AEI-type AlPO–18 zeolite membranes were prepared on macroporous mullite and two–layer \( \alpha - \text{Al}_2\text{O}_3 \) tubes with less expensive N, N–disopropylethylamine (DIPEA) as a single template. The obtained membranes by single DIPEA template showed both high CO\(_2/\)CH\(_4\) and N\(_2/\)CH\(_4\) perm–selectivities and fluxes. The membrane prepared on two–layer \( \alpha - \text{Al}_2\text{O}_3 \) support showed a CO\(_2\) single gas permeance as high as \( 4.2 \times 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1} \) with the perm–selectivity of 90 for CO\(_2/\)CH\(_4\) at 298 K and 0.11 MPa. Besides, a compatible N\(_2/\)CH\(_4\) perm–selectivity of 8.1 with N\(_2\) single gas permeance of \( 1.5 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1} \) at 298 K and 0.11 MPa was obtained from the membrane prepared on macroporous mullite support. Although a few of AFI type AlPO–5 impurities were formed on the surface of those AlPO–18 zeolite membranes, the AFI impurities didn’t lower the gas permeation performance.

Keywords : AEI type AlPO–18 zeolite membrane / single DIPEA template / gas permeation

1. Introduction

The separation of CO\(_2\) and N\(_2\) from other components, such as CH\(_4\), typically present in natural gas wells is of importance since both decrease the energy content of the gas, and meanwhile CO\(_2\) is corrosive in the presence of moisture. Carbon dioxide can be removed with amine scrubbers or polymer membranes. The amine scrubbers require high pressure and thus they are relatively expensive, and the selectivity of polymer membranes decreases at high pressure due to the plasticization from dissolved CO\(_2\). Cryogenic distillation allows the separation of N\(_2\) but energy costs are high \(^1\). Membrane separation with inorganic membranes that have molecular–sized pore and good thermal, hydrothermal stabilities is thus of interest for natural gas separation, as energy requirements are low and they are not susceptible to plasticization. Several types of zeolite membranes such as T \(^2\), DDR \(^3\), SAPO–34 \(^4\), \(^5\), Si–CHA \(^6\), SSZ–13 \(^5\), \(^6\), SAPO–17 as well as AlPO–17 \(^7\), AlPO–18 \(^8\), \(^9\) and the MOF material ZIF–8 \(^10\) have been investigated for CO\(_2\) separation. The SAPO–34 \(^1\), \(^5\), \(^11\) – \(^13\), SSZ–13 \(^9\), and AlPO–18 \(^10\) zeolite membranes also have N\(_2/\)CH\(_4\) selectivity that are above to the upper bound of the Robeson plot \(^15\) that is commonly used to compare polymers membranes.

AlPO–18 is an aluminophosphate zeolite with the AEI–type framework that is formed from equimolar AlO\(_4\) and PO\(_4\) tetrahedral units. It has three–dimensional, electrically neutral pores with a diameter of 3.8 Å, indicating the potential for separating CO\(_2\) (3.3 Å) and N\(_2\) (3.64 Å) from CH\(_4\) (3.8 Å) by molecular sieving. The Carreon group \(^14\), \(^16\) showed that AlPO–18 zeolite membranes can separate both CO\(_2/\)CH\(_4\) and N\(_2/\)CH\(_4\) mixtures. The CO\(_2/\)CH\(_4\) separation was further improved by Wang et al. \(^8\) with a CO\(_2\) permeance of \( 6.5 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1} \) (\( \sim 1940 \text{ GPU} \)). This permeance was still lower than the highest permeances reported for SAPO–34 membranes \(^4\) but the N\(_2\) fluxes \(^14\) for N\(_2/\)CH\(_4\) separation were higher than those previously reported for SAPO–34 membranes, while, the N\(_2/\)CH\(_4\) selectivity was lower than that of the SAPO–34 membranes \(^12\). Furthermore, the AlPO–18 zeolite membranes were conventional prepared

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through the high cost tetraethylammonium hydroxide template (TEAOH). In the view of low cost to industrial application, less expensive DIPEA template is cost-saving towards preparing the AlPO–18 zeolite membranes. Hasegawa et al. \(^{17}\) successfully fabricated the AEI type AlPO–18 zeolite membranes by single DIPEA for H\(_2\)O/EtOH separation, while the gas permeations have not been discussed.

In this work, we prepared the AEI zeolite membranes with single and less expensive DIPEA template. The effects of temperature ranges from 298 K to 473 K and pressure from 0.11 to 0.40 MPa on the permeation of AEI membranes were also investigated.

2. Experimental

2.1 Preparation of AEI type AlPO–18 zeolite membranes

The AEI membranes were prepared by secondary growth on the outside of porous mullite tubes (12 mm OD, 9 mm ID and 1.3 µm average pore size, Nikkato Co.) and two–layer porous \(\alpha\)-\(\text{Al}_2\text{O}_3\) supports (12 mm OD, 9 mm ID, 100 nm/2.1 µm average pore size, Nikkato Co.) with the gel composition of 1.0 \(\text{Al}_2\text{O}_3\) : 1.0 \(\text{P}_2\text{O}_5\) : (1.0 ~ 1.8) DIPEA : 120 H\(_2\)O, where the DIPEA is N, N–diisopropylethylamine. The gel solution was prepared by mixing Al(i–C\(_3\)H\(_7\)O)\(_3\) (98%, Sigma–Aldrich), \(\text{H}_3\text{PO}_4\) (85 wt.% aqueous solution, Wako) and deionized water and stirred for 3 h at room temperature to form a homogeneous solution. Then the DIPEA (99 wt.%, TCI.co) was added drop-wise. The resulting solution was then stirred for 12 h. The rub–coating seeded supports were placed vertically into an autoclave and the synthesis gel was slowly added. Zeolite growth was carried out under hydrothermal conditions at 478 K for 48 h. Here, the AEI–type AlPO–18 crystals prepared as described previously \(^9\) were used as the seed and rubbed onto the outer surface of porous tubes. After synthesis, the AEI membranes were washed under running tap water, then rinsed and soaked until the soaking solution was clear. The membranes were dried in an oven at 353 K and then calcined in air at 753 K for 6 h with heating and cooling rates of 0.5 K/min.

2.2 Characterization

The morphologies of as–synthesized AEI membranes were determined by a field emission scanning electron microscope (FE–SEM, JEOL JSM 6335 F) at an acceleration voltage of 5 KV. The crystallinity of the AEI membranes was identified by X–ray diffraction (XRD) using a RIGAKU Smart Lab 9/SWXD diffractometer with Cu–K\(\alpha\) radiation at a scanning range of 2 \(\theta\) from 5 to 45° and a scanning rate of 4°/min.

2.3 Single gas permeation measurements

Single gas permeation of He, H\(_2\), CO\(_2\), O\(_2\), N\(_2\), CH\(_4\), CF\(_4\) and SF\(_6\) was measured between 298 K and 473 K under vacuum using the time–lag method with fixed–volume apparatus as described previously \(^{18}\). The membranes were mounted in a stainless–steel cell and sealed with 4 rubber o–rings and 2 stainless steel rings on both ends. The area of the membranes was 18.9 cm\(^2\). Before the permeation measurements, the membrane was degassed at 473 K for 20 h. For the permeation measurements, the test gas was introduced to the feed side with a back–pressure regulator. The pressure increase on the fixed–volume permeate side due to the gas permeation was monitored with a pressure transducer after closing the vacuum line to the permeate volume. The permeance (P) was then calculated from the pressure increase and the known cell volume on the permeate side. Ideal selectivity (\(\alpha\)) for different gas pairs was calculated as the ratio of the single gas permeances.

3. Results and discussion

3.1 Characterization

AEI membranes prepared with n(DIPEA) of 1.0 ~
Membrane AEI membranes prepared with different synthesis conditions and gas permeation properties at 308 K and 0.11 MPa

<table>
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<tr>
<th>Membrane</th>
<th>Support</th>
<th>n (DIPEA)</th>
<th>Syn. Conditions</th>
<th>Phase</th>
<th>Permeance [10^{-7} mol m^{-2} s^{-1} Pa^{-1}]</th>
<th>Ideal selectivity α [-]</th>
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<td>478K, 36h</td>
<td>AEI</td>
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<th>Syn. Conditions</th>
<th>Phase</th>
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<td>AEI</td>
<td>7.42 0.61 0.10</td>
<td>71.2 5.85</td>
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Gel composition: 1.0Al2O3: 1.0P2O5: n (DIPEA or TEAOH): 120H2O

Fig. 2 Surface (a) and cross section (b) of membrane AEI–3, cross section (c) of membrane AEI–9.

1.8 under 478 K for 48 h were summarized in Table 1. In comparison, two AEI type AlPO–18 zeolite membranes (M–1 and M–2) were prepared by TEAOH template with the similar procedures as our previous reported. The corresponding synthesis conditions and gas permeation results are also displayed in Table 1. XRD patterns of as–synthesized membranes M–1, AEI–3 on mullite support by 1.0 DIPEA and membrane AEI–9 on α–Al2O3 support by 1.2 DIPEA after calcination are shown in Fig. 1. All three membranes show the characteristic peaks of the AEI zeolite, while AFI type AlPO–5 impurity with the characteristic peak at ~ 7.4° is formed on those membranes prepared by single DIPEA template. AlPO–5, with the AFI type framework, is another microporous aluminophosphate with one dimensional, cylindrical pores, owns a diameter of 7.3 Å that was much bigger than the kinetic diameter of CO2, N2 and CH4. Thus permeances of AlPO–5 membranes are much higher but selectivities are low. It has been reported that the competing phase of AFI formed at n(DIPEA/P2O5) < 1.2 when preparing AEI type SAPO–18 zeolite with DIPEA template. Although Hasegawa et al. claimed that high temperature favors to form AFI impurity on AEI membranes when using single DIPEA template, pure AEI membranes can be obtained by shortening synthesis time to
The as-synthesized membrane AEI–3 on mullite support has a compact and continuous layer covering the support surface with the thickness of $\sim 12 \mu m$ as shown in SEM (Fig. 2b). Plate–shaped AEI crystals morphologies with the size of $\sim 1 \mu m$ were covered on the top of the surface as shown in Fig. 2a, which is smaller than the pore size of the mullite support. The AFI type crystals with hexagonal morphology were stuck into the membrane layer. On the contrary, the membrane AEI–9 prepared on two–layer $\alpha$–Al$_2$O$_3$ support displayed the continuous zeolite layer with the thickness of $\sim 4.5 \mu m$ as shown in Fig. 2c, which is less than half of the membrane prepared on mullite support. The difference of the membrane thickness on alumina and mullite supports may due to the structural properties of these supports. The 0.1 $\mu m$ average pore size layer of alumina support may provide a smoother surface than that of 1.3 $\mu m$ mullite support $^6$, which results in a thinner seeded layer after seeding the supports. It may improve the gas permeance compared with thicker zeolite separation layer on mullite support (Fig. 2b and Table 1). At the same time, some voids were formed within the membrane layers on both mullite and $\alpha$–Al$_2$O$_3$ supports, it may also improve the permeances.

3.2 Single–gas permeation

Fig. 3 shows single gas permeances of the membranes AEI–3 and AEI–9 at 308 K and 0.11 MPa as a function of kinetic diameter of gases. The single gas permeances of membrane M–1 are also shown in Fig. 3. The variations in permeances for three membranes are similar to each other with the order of $CO_2 > H_2 > He > O_2 > N_2$ as described in our previous study $^9$. These gases seem to permeate into the AEI zeolite pores. $CO_2$ shows the highest permeances although its molecular weight is higher than those four gases, which suggests adsorption selectivity. On the other hand, the permeance of $CH_4$ with relatively low molecular weight is lower than the permeances of those five gases. This is due to the molecular sieving effect. The AEI zeolite membrane, therefore, is quite suitable for $CO_2/CH_4$ and $N_2/CH_4$ separations.

$CF_4$ (4.7 Å) and $SF_6$ (5.5 Å), which were much larger than the AEI zeolite pores, are also permeated a little through those prepared membranes. This seems due to the presence of a few defects, which may be at crystal grain boundaries. However, as the permeances are 1/5 or 1/10 of that to $CH_4$, it can be concluded the membranes AEI–3 and AEI–9 have few defects. These membranes prepared with DIPEA display higher gas permeability than the membranes prepared with TEAOH, which may be attributed to the AFI type crystals. The presence of impurity AFI crystals in membrane AEI–3 and AEI–9 may reduce the effective thickness of zeolite layer. The AEI membranes on the two-layer alumina tubes exhibit higher gas permeability than that on mullite tubes. It may due to thinner zeolite layer as shown in Fig. 2.

3.3 Temperature dependence of permeation

Temperature dependence ranges from 298 K to 473 K on the single gas permeances through membranes AEI–3 and AEI–9 at 0.11 MPa is shown in Fig. 4. The effect of temperature on single gas permeances for both two membranes are similar although membrane AEI–9 shows much higher gas permeance than AEI–3. The permeances of $CO_2$, $O_2$ and $N_2$ are strongly affected by temperature. These permeances continuously decreased, while the permeances of $He$, $H_2$ and $CH_4$ were almost independent to the temperature. The permeance of $SF_6$ slightly increased with increasing the temperature. The activation energy of $SF_6$ calculated from Arrhenius equation for membrane AEI–3 was +4.7 kJ/mol, indicates the activated diffusion of the $SF_6$ through the membrane. Since the AEI pore size (0.38 nm) is smaller than the $SF_6$ (0.55 nm), the permeance may due to the non–zeolite pores in the membrane.
The calculated $H_2/CH_4$, $CO_2/CH_4$, $CO_2/N_2$ and $N_2/CH_4$ ideal selectivities of membranes AEI–3 and AEI–9 are shown in Fig. 5 as a function of temperature. The perm–selectivity of $CO_2/CH_4$, $CO_2/N_2$ and $N_2/CH_4$ for both two membranes decreased dramatically with increasing temperature from 298 K to 473 K. The $CO_2$ single gas permeance decreased by 86% from $1.58 \times 10^{-6}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ at 298 K to $2.20 \times 10^{-7}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ at 473 K with the $CO_2/CH_4$ ideal selectivity decreased from 87.4 to 13.4 for membrane AEI–3, and the $CO_2$ permeance decreased by 88% from (4.17 to 0.52) $\times 10^{-6}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ for AEI–9 with the $CO_2/CH_4$ ideal selectivity decreased from 89.6 to 12.3.

At 298 K, the $N_2/CH_4$ ideal selectivity was 8.1 (Fig. 5a) with a $N_2$ single gas permeance of $1.46 \times 10^{-7}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ for AEI–3 and 6.1 with $N_2$ single gas permeance of $2.82 \times 10^{-7}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ for AEI–9. Even though AlPO–18 preferentially adsorbs $CH_4$ over $N_2$ (14), molecular sieving affect may result in preferentially permeation of $N_2$ over $CH_4$. The $N_2$ single gas permeance decreased to $0.46 \times 10^{-7}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ for AEI–3 and $0.98 \times 10^{-7}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$ for AEI–9 at 473 K with the $N_2/CH_4$ ideal selectivity of 2.8 for AEI–3 and 2.3 for AEI–9.

### 3.4 Pressure dependence of permeation

Fig. 6 shows the changes in gas permeance for $CO_2$, $N_2$ and $CH_4$ as well as the corresponding perm–selectivity for $CO_2/CH_4$ and $N_2/CH_4$ through membrane AEI–3 and AEI–9 as a function of feed pressure at 308 K. But for membrane AEI–9, it is difficult to measure permeance of $CO_2$ due to the permeance that beyond the limit of equipment. For membrane AEI–3, the $CO_2$ permeance decreased when increasing pressure from 0.11 MPa to 0.4 MPa, whereas both the $N_2$ and $CH_4$ permeance increases slightly with pressure,
therefore, the CO₂/CH₄ and N₂/CH₄ perm-selectivity dropped to 62.8 and 6.76 at 0.4 MPa, respectively.

3.5 Comparison

Fig. 7 shows plots of $P_{CO_2}$ vs $\alpha$ (CO₂/CH₄) and $P_{N_2}$ vs $\alpha$ (N₂/CH₄) of the AEI membranes prepared with single TEAOH and DIPEA template at 0.11 MPa and 298 K. Compared with the reported CO₂/CH₄ separation membranes, highest CO₂ single gas permeance of $4.17 \times 10^{-6}$ mol m⁻² s⁻¹ Pa⁻¹ was obtained by using less expensive DIPEA template with the ideal selectivity of 89.6 for AEI-9 on two-layer $\alpha-\text{Al}_2\text{O}_3$ support. However, for the N₂/CH₄ separation, the separation performance is still lower than the reported data, although membrane AEI-3 prepared on mullite support showed a compatible N₂/CH₄ selectivity of 8.08 with the N₂ permeance of $1.46 \times 10^{-7}$ mol m⁻² s⁻¹ Pa⁻¹. More studies should be performed to optimize the synthesis conditions in order to obtain high-performance AEI membranes.

4. Conclusion

The AEI membranes were prepared with DIPEA as single and less expensive template using a gel composition of 1 Al₂O₃ : 1 P₂O₅ : (1.0 ~ 1.8) DIPEA : 120 H₂O. Minority AFI impurity was formed on the surface of AEI membranes, however, it didn’t affect CO₂/CH₄ and N₂/CH₄ separations. These membranes displayed a much higher gas property than the membranes prepared by single and expensive TEAOH template. Membrane prepared on two-layer $\alpha-\text{Al}_2\text{O}_3$ support showed CO₂ single gas permeance as high as $4.2 \times 10^{-6}$ mol m⁻² s⁻¹ Pa⁻¹ with the perm-selectivity up to 90 for CO₂/CH₄. Membrane prepared on mullite support
displayed a compatible N₂/CH₄ selectivity of 8.1 with the N₂ gas permeance of 1.5 × 10⁻⁷ mol m⁻² s⁻¹ Pa⁻¹ and at 298 K and 0.11 MPa.

CO₂ and N₂ single gas permeances were strongly affected by temperature and pressure, while CH₄ was almost independent for these AEI membranes.

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