A new superior competitor for exceptional propylene/propane separations: ZIF-67 containing mixed matrix membranes

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Abstract

Recently, the ZIF-67 molecular sieve has emerged as an excellent substitute for the ZIF-8 counterpart due to its potentially high C_3H_6/C_3H_8 separation performance. Here, for the first time, we investigated the effect of ZIF-67 in mixed matrix membranes (MMMs) for C_3H_6/C_3H_8 separations by integrating them into 6FDA-DAM polymeric matrix. The 6FDA-DAM/ZIF-67 (80/20 wt/wt) MMMs achieved an ideal selectivity of 29.9 and a separation factor of 19 under single and equimolar mixed gas conditions, respectively, at 35 °C. The intrinsic C_3H_6/C_3H_8 separation performance of ZIF-67 was estimated from our experimental transport results based on the Maxwell model. The calculation demonstrated its superior C_3H_6/C_3H_8 selectivity of 251, which is twice of that of ZIF-8, supporting the high molecular sieving capacity of ZIF-67 containing MMMs. Moreover, a thorough investigation on the temperature-dependent gas transports elucidated that the energetic selectivity is a major contributor for the high C_3H_6/C_3H_8 diffusivity selectivity in ZIF-67 containing MMMs, although the minimum aperture size of 4.5 Å of ZIF-67 substantially sacrificed the C_3H_6/C_3H_8 entropic selectivity. Lastly, the defect-free incorporation of ZIF-67 nanoparticles into 6FDA-DAM polymer matrix effectively retarded physical aging process, maintaining the excellent separation performance of the associated MMMs for 75 days.

Keywords: ZIF-67; 6FDA-DAM; mixed matrix membranes; propylene/propane separations; physical aging resistance

1. Introduction

Propylene/propane separation is one of the most important processes in the petrochemical industry, due to the highly utile applications of both gases in our everyday life [1]. Propylene is the second most important feedstock next to ethylene with its annually increasing demands: the 90 million tons of global demand in 2014 was expected to continually increase, exceeding 130 million tons in 2023 based on IHS Chemical North American Propylene Supply Study [2]. Currently, propylene/propane (i.e., C_3H_6/C_3H_8) separation is implemented mainly by highly energy-intensive cryogenic distillation due to the similar physical properties between C_3H_6 and C_3H_8 (i.e., T_b of C_3H_6 and C_3H_8 is $-47.6\text{ }^{\circ}\text{C}$ and $-42.1\text{ }^{\circ}\text{C}$, respectively) [3]. Therefore, the energy-efficient alternatives have been actively sought-out for the C_3H_6/C_3H_8 separations.

Membrane-based separation technique is promising due to its good energy efficiency as well as low capital cost. Conventional polymeric membranes, however, have been yet to reach and/or surpass the performance limit *so-called* “the upper bound” [4], albeit their great advantage of high processability. A number of different approaches have been attempted to achieve high C_3H_6/C_3H_8 separation performances. While facilitated transport membranes showed prominent performances for C_3H_6/C_3H_8 separations, their poor long-term stability severely depressed the practical utilization [5, 6]. Among the diverse strategies, using molecular sieve materials has drawn a great attention due to their excellent and stable C_3H_6/C_3H_8 separation performances. Nevertheless, the inorganic membranes composed of molecular sieves such as zeolite [7] and metal organic framework (MOF) [8] have yet to control the formation of non-selective grain boundary microstructures [9], making it difficult to use those materials solely. Instead, by embedding selective inorganic molecular sieves into

polymeric materials, the composite membranes referred to as mixed matrix membranes (MMMs) have demonstrated a promising potential for C₃H₆/C₃H₈ separations [10].

Despite many advantages of MMMs, the non-ideal morphology issues of MMMs are still challenging impediments including particle agglomerations or formation of interfacial voids caused by poor wetting of particles by polymer matrix in the development of MMMs [11]. Also, selection of appropriate molecular sieves whose transport properties are matched up with those of polymer matrix is an arduous task to achieve high separation performance of MMMs [12]. Among many previous studies of MMMs for C₃H₆/C₃H₈ separations, Zhang et al. [13] successfully demonstrated the excellent C₃H₆/C₃H₈ separation performance of MMMs by using 6FDA-DAM polyimide and zeolitic imidazolate framework (ZIF-8). Due to the flexibility of organic linkers, the effective pore size of ZIF-8 was evaluated to be larger than its apparent pore size (i.e., 3.4 Å) and suitable for C₃H₆/C₃H₈ separations [14].

Very recently, Kwon and colleagues substantially improved C₃H₆/C₃H₈ separation performance by heteroepitaxially growing ZIF-67 (Co-substituted ZIF-8) on ZIF-8 seed layers [15]. They suggested that ZIF-67 might be intrinsically more efficient than ZIF-8 for C₃H₆/C₃H₈ separation due to the stiffer Co-N bond as compared to the Zn-N bond in ZIF-8. Also, Krokidas and co-workers [16] further confirmed that ZIF-67 is more efficient for C₃H₆/C₃H₈ separations based on their newly-developed force fields and subsequent molecular dynamics simulations. It is interesting that besides more-commonly observed linker-substitution, metal-substitution also affects the molecular sieving efficiency of the associated ZIF crystals.

In this work, we demonstrated the high C₃H₆/C₃H₈ separation performance of ZIF-67 containing MMMs by using defect-free 6FDA-DAM/ZIF-67 MMMs for the first time. The

MMMs showed superior C₃H₆/C₃H₈ separation performances for single gas as well as mixed gas, far exceeding the upper bound limit for polymeric membranes. Also, our thorough investigation on the separation performance of ZIF-67 containing MMMs allows to estimate the inherent separation performance of ZIF-67 for C₃H₆/C₃H₈ separations. Moreover, the temperature-dependent gas transport characterizations were performed to systematically analyze the molecular sieving mechanism. Finally, the influence of the ZIF-67 nanoparticles on the physical aging of MMMs was carefully investigated.

2. Theory and background

Gas separation membranes have two important parameters to evaluate their separation performance: permeability and permselectivity. Permeability is defined as a flux of gas penetrants through membranes normalized by given pressure and membrane thickness.

$$P_i = \frac{N_i \times l}{p_2 - p_1} \quad (1)$$

Where P_i and N_i are the permeability and the flux of gas i , respectively. l is the thickness of membrane and p_1 and p_2 are the pressure of downstream and upstream, respectively. The common unit for permeability is Barrer and defined as:

$$1 \text{ Barrer} = 10^{-10} \frac{\text{cm}^3(\text{STP}) \text{ cm}}{\text{cm}^2 \text{ s cmHg}} \quad (2)$$

The gas transport of dense polymeric membranes is based on the solution-diffusion mechanism. Permeability can be expressed by the product of diffusivity (D_i) for kinetic factor and solubility (S_i) for thermodynamic factor [17].

$$P_i = D_i \times S_i \quad (3)$$

Sorption isotherms in glassy polymers are described by the dual-mode model. This model can be represented by the Henry's law mode and the Langmuir mode: the equilibrium and non-equilibrium structures [18].

$$S_i = \frac{C_i}{p_i} = k_{D,i} + \frac{C'_{H,i} \times b_i}{1 + b_i \times p_i} \quad (4)$$

Where C_i is the concentration of gas i in polymer, p_i is the partial pressure. $k_{D,i}$ is the Henry's constant for Henry's law mode, $C'_{H,i}$ is the Langmuir sorption capacity, and b_i is the Langmuir affinity constant. Also, for microporous molecular sieves with a finite number of sorption sites, the solubility is expressed only by the Langmuir mode as follow.

$$S_i = \frac{C_i}{p_i} = \frac{C'_{H,i} \times b_i}{1 + b_i \times p_i} \quad (5)$$

For single gas separations, the permselectivity ($\alpha_{i/j}$) is simply defined as the ratio of the permeability of gas penetrant i over that of j . Also, the permselectivity can be expressed in terms of diffusivity selectivity and solubility selectivity as follows:

$$\alpha_{i/j} = \frac{P_i}{P_j} = \frac{D_i}{D_j} \times \frac{S_i}{S_j} \quad (6)$$

Since diffusion of gas penetrants in polymer is a thermally activated process, it requires the energy barrier, the *so-called* activation energy for diffusional jumps. The temperature dependence of diffusivity is expressed in Arrhenius equation form.

$$D_i = D_{o,i} \exp\left(-\frac{E_{D,i}}{RT}\right) \quad (7)$$

Where $D_{o,i}$ is a pre-exponential factor of diffusivity, $E_{D,i}$ is an activation energy for diffusion, R is the universal gas constant, and T is the temperature. Temperature dependence of solubility can be expressed by van't Hoff equation.

$$S_i = S_{o,i} \exp\left(-\frac{H_{S,i}}{RT}\right) \quad (8)$$

Where $S_{o,i}$ is a pre-exponential factor of solubility, $H_{S,i}$ is a heat of sorption, generally negative. From Equations (3), (7), and (8), temperature dependence of permeability is described as:

$$P_i = P_{o,i} \exp\left(-\frac{E_{P,i}}{RT}\right) \quad (9)$$

where

$$P_{o,i} = D_{o,i} \times S_{o,i} \quad (10)$$

$$E_{P,i} = E_{D,i} + H_{S,i} \quad (11)$$

3. Experimental

3.1. Materials

6FDA-DAM with a molecular weight of ca. 220,000 g/mol was purchased from Akron Polymer Systems. N-Methyl-2-pyrrolidone (NMP, extra pure, Daejung Chemical Co. LTD) was used as a solvent for the membrane fabrications. Cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$)

6H₂O, 98%, Sigma-Aldrich) and 2-methylimidazole (C₄H₆N₂, 99%, Sigma-Aldrich) were used for the synthesis of ZIF-67 nanoparticles without further purification.

3.2. Preparation of ZIF nanoparticles

Commercially available ZIF-8 particles (Basolite Z1200, Sigma-Aldrich) were used in this work. ZIF-67 nanoparticles were synthesized by modifying a literature procedure [15]. ZIF-67 particles were synthesized at room temperature by intensively mixing a cobalt metal source solution containing deionized (DI) water of 8 g and cobalt nitrate hexahydrate of 1.17 g with a ligand source solution containing DI water of 80 g and 2-methylimidazole of 22.70 g for 5 min. Then, an aging step was followed sequentially at room temperature for 12 h. The homogeneous purple mixture was centrifuged at 8000 rpm for 30 min and decanted. To remove all the residual solvent and unreacted species, the prepared nanoparticles were washed in fresh methanol at least three times and then dried at 100 °C under vacuum for 12 h before use.

3.3. Fabrication of dense films

6FDA-DAM powders were dried at 100 °C under vacuum for 12 h to remove any solvent. They were dissolved in NMP with an appropriate concentration. The polymer solutions were rolled for 12 h to obtain completely homogeneous solutions. Neat polymeric membranes were fabricated by using a knife-casting method on the flat and clean glass plate and then immediately dried at 180 °C under vacuum for 12 h. The formed thin films were peeled off from the glass plate and further dried at the same conditions for 12 h. Molecular sieve-containing polymer solutions were prepared by the “priming” method, which can be found elsewhere [19]. Each particle was dispersed in 70 wt % of the total NMP by water bath sonicator (MUJIGAE, South Korea) with a power of 100 W for 1 h. It should be noted that the

interaction between nanoparticles and solvent plays a role in uniformly dispersing nanoparticles in solvent [20]. Our previous work exhibited that commercial ZIF-8 particles were well-dispersed in NMP while they were agglomerated in both chloroform (CHCl_3) and tetrahydrofuran (THF) [20]. Since ZIF-67 involves the same organic ligands as those for ZIF-8, NMP was chosen as the solvent for the MMMs. Also, a horn type sonicator was avoided because ZIF particles can form agglomerates by the Ostwald ripening effect at this step [21]. The dilute “priming” dope containing 30wt% of the total NMP and 15wt% of the total 6FDA-DAM powders was added into suspensions. Remaining 85 wt% of the total 6FDA-DAM was added into the mixture after the dope turned homogeneous. The prepared composite solution was treated by the same procedure as the one for neat polymeric membranes to fabricate mixed matrix membranes.

3.4. Transport characterization

Single gas permeation measurements were preceded by a standard isochoric technique [22] at 2 atm and at three different temperatures (i.e., 35, 50, and 70 °C) using the gases with purity of 99.95 %. The permeation test for each type of sample was carried out by using at least four different films from at least four individual fabrications. Each permeation test was conducted after verifying the air leakage rate of permeation systems was less than 1% of the steady state permeation rates. More detailed procedures were described in elsewhere [23]. Also, all the permeation tests were performed as soon as membranes were fabricated except those for the aging study. Samples for the aging study were stored in vacuum condition at 25 °C for the considered aging time. Mixed gas permeation measurements were performed for $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ binary gas mixture (50/50 mol/mol) at C_3H_6 partial pressure of 2 atm and 35 °C. The stage cut, which is the percentage of the feed that permeates through the membrane, was controlled less

than 1 % in order to prevent concentration polarization [24]. The composition of permeates was analyzed by gas chromatography (GC, 7890B (Agilent)). Equilibrium sorption isotherms of C₃H₆ and C₃H₈ in ZIF-67, ZIF-8 nanoparticles, 6FDA-DAM, and ZIF-67 containing MMMs were evaluated at 35 °C by using the pressure decay method [25].

3.5. Supplementary characterization

Field emission gun scanning electron microscopy (FEG-SEM, Inspect F (FEI)) was employed with 10 kV to characterize the morphology of our synthesized ZIF-67 nanoparticles as well as MMMs. Fourier transform infrared spectroscopy (FT-IR, FT-IR frontier (Perkin-Elmer)) was used to evaluate interactions between 6FDA-DAM polymer and ZIF-67 in MMMs over the range of 4000-400 cm⁻¹. Wide angle X-ray diffraction (WAXD, D/Max 2500/PC (Rigaku)) was used to verify the phase and crystallinity of ZIF-67 nanoparticles with Cu-K α radiation ($\lambda=1.5406$ Å). The glass transition temperature (T_g) of membranes was analyzed by using differential scanning calorimetry (DSC, Q20 TA instruments) to investigate change of polymer chain mobility with the incorporation of ZIF-67. Each sample was heated from 25 °C to 100 °C at a ramp rate of 5 °C/min under N₂ purge of 50 ml/min. The samples were heated at 100 °C for 30 min to remove any moisture and then were heated to 410 °C at the same condition. Thermo gravimetric analysis (TGA, TGA1 (METTLER TOLED)) was performed to determine the actual content of ZIF nanoparticles in MMMs. More specifically, TGA was run from 25 °C to 800 °C with a heating rate of 5 °C/min under air atmosphere (50 cm³/sec), fully transforming the samples to cobalt oxide (CoO). The residual cobalt (Co) weight percentage of ZIF-67 was comparable with the theoretical weight percentage of Co in ZIF-67 nanoparticles (i.e., 26.4 %). As such, the actual weight percentages of ZIF-67 in MMMs were calculated by the ratio of Co wt% of MMM to that of ZIF-67 [13].

4. Results & Discussion

4.1. Characterization of ZIF-67 nanoparticles

The house-made ZIF-67 nanoparticles showed a uniform particle size of 300 – 400 nm with dodecahedral shapes (Fig. 1a). As shown in Fig. 1b, the FT-IR spectra of ZIF-67 indicated covalent bonds between cobalt and nitrogen of 2-methylimidazole (2-MIM) ligands at the designated wavenumber of 426 cm^{-1} [15]. The XRD patterns of ZIF-67 exhibited a typical sodalite (SOD) topology (Fig. 1c) with theoretical aperture size of $\sim 3.3\text{ \AA}$ [16]. Nevertheless, due to the flexible 2-methylimidazolate (2-mIM) ligands in ZIF-67, the effective aperture size is anticipated to be larger than the theoretical one similarly to the case of ZIF-8, whose theoretical pore size is $3.4\text{ \AA}$ but the effective pore size is found between 4.0 and $4.2\text{ \AA}$ [14]. Also, the equilibrium sorption isotherms of C_3H_6 and C_3H_8 for ZIF-67 nanoparticles were characterized at $35\text{ }^\circ\text{C}$ (Fig. 1d). As represented in Fig. 1d, the sorption capacities of C_3H_6 and C_3H_8 for ZIF-67 nanoparticles are analogous; therefore, the $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ sorption selectivity was 1.1 at 29.3 psia. The equilibrium sorption isotherm data for both C_3H_6 and C_3H_8 in ZIF-67 were fitted well with the Langmuir model in Equation (5) and the associated parameters are summarized in Table S1. Both Langmuir sorption capacity, C_H' and Langmuir affinity constant, b for each penetrant in ZIF-67 were very similar to those for ZIF-8 within the experimental uncertainties. It reflects that the accessible micro-voids and affinities of ZIF-67 for C_3H_6 and C_3H_8 are comparable with those of ZIF-8 (Table S1), despite the different transition metals connected with 2-mIMs (i.e., Co for ZIF-67 vs. Zn for ZIF-8).

Fig. 1. ZIF-67 nanoparticle characterizations: SEM (a), FT-IR (b), XRD (c), and sorption isotherm for C₃H₆ and C₃H₈ (d) at 35 °C.

4.2. Physical properties of ZIF-67 containing MMMs

ZIF-67 nanoparticles were well-dispersed in the 6FDA-DAM (PI) polymer matrix up to nominal concentration of 20 wt% with the assistance of proper ultra-sonication treatments while mitigating the Ostwald ripening [21]. As shown in Fig. 2, the uniformly distributed ZIF-67 nanoparticles showed good adhesion with PI. It should be noted that ZIF-67 particles at the concentration of 30 wt% started to agglomerate in MMMs with a selectivity loss of 10%. This is likely due to the fact that the van der Waals interactions between ZIF-67 particles are stronger than the interaction of ZIF-67 particles with either polymer or solvent (Fig. S1) [11, 26]. Such non-ideal morphology is detrimental to the separation performance because gas penetrants prefer to bypass through the non-resistant void volumes formed within the agglomerates regardless of their sizes. Nevertheless, our 6FDA-DAM/ZIF-67 MMMs with up to 20 wt% of ZIF-67 exhibited that the formation of ZIF-67 clusters was efficaciously mitigated probably

due to a combination of the selection of an appropriate solvent (i.e., NMP) and the exclusion of direct sonication. For the sake of convenience, the ZIF-67 containing MMMs used in this work were named as a function of ZIF-67 contents: PZ67-10 for PI/ZIF-67 (90/10 wt/wt) and PZ67-20 for PI/ZIF-67 (80/20 wt/wt).

Fig. 2. Cross-sectional SEM images of PZ67-10 (a) and PZ67-20 (b).

Specific interaction between 6FDA-DAM and ZIF-67 nanoparticles was investigated by conducting FT-IR analysis. The FT-IR spectra of ZIF-67 MMMs were almost identical to

those of the neat 6FDA-DAM (Fig. S2), confirming that no specific interaction exists between 6FDA-DAM and ZIF-67. This is not surprising since 6FDA-DAM/ZIF-8 MMMs also showed no specific interaction between 6FDA-DAM and ZIF-8 which involves the same organic ligand of 2-mIM [27]. Nevertheless, the 2-mIM-induced hydrophobic properties of ZIF-67 nanoparticles allow a good affinity with the polymer matrix, suppressing the formation of interfacial voids [13]. Despite the lack of specific interaction, the strong affinity between polymer matrix and dispersed particles tends to rigidify the polymer matrix around the embedded particles [27]. As shown in Fig. S3, the glass transition temperature (T_g) of PI (i.e., 371 °C), which is consistent with the reference value [28], increased upon the addition of ZIF-67 nanoparticles into the polymer matrix. While the rigidification of polymer chains itself can induce changes in separation performance (typically decreasing permeability with increasing selectivity), its effect on the inherently rigid polymer with high T_g is generally negligible [29].

As the gas separation performances of MMMs depend highly on the amount of embedded particles, the actual contents of ZIF-67 in MMMs are important for the accurate characterization of gas transport in MMMs [30]. The residual weight percentages of ZIF-67 and their MMMs were characterized using TGA, (Fig. S4) and the corresponding percentages of ZIF-67 in MMMs are shown in Table S2. The actual ZIF-67 concentrations in MMMs are nearly comparable with the nominal ones as shown in Table S2.

4.3. Gas transport properties of ZIF-67 containing MMMs

4.3.1. C₃H₆/C₃H₈ separation performances

Both C₃H₆ and C₃H₈ single gas transport behaviors in pristine 6FDA-DAM (PI) and ZIF-67 containing MMMs were characterized at 2 atm and 35 °C and the corresponding results

are summarized in Table 1. The C_3H_6 and C_3H_8 permeabilities in PI are 16.63 and 1.47 Barrer, respectively, consistent with the reference values within the experimental uncertainties (i.e., C_3H_6 permeability: 15.7 Barrer and C_3H_8 permeability: 1.27 Barrer) [13]. In MMMs, the C_3H_6/C_3H_8 separation performance was continually improved with increasing the content of ZIF-67, overcoming the polymeric upper bound limit for C_3H_6/C_3H_8 separations (Fig. 3) [4]. Both C_3H_6 permeability and C_3H_6/C_3H_8 permselectivity of PZ67-20 increased by as much as 105.3 % and 164.6 %, respectively, comparing with those of PI. Interestingly, the C_3H_8 permeability decreased with increasing ZIF-67 concentrations in MMMs, which is attributed to the realization of molecular sieving effect of ZIF-67 for C_3H_8 gas molecules, significantly increasing the C_3H_6/C_3H_8 permselectivity. It should be noted that the realization of molecular sieving effect of ZIF-67 in MMMs was due to a proper match with respect to the permeable behaviors between PI and ZIF-67 as well as a good interfacial adhesion between them.

Furthermore, C_3H_6/C_3H_8 separation performances for PI/ZIF-67 MMMs were compared to those for PI/ZIF-8 counterparts, since ZIF-8 nanoparticles are known to be the most appropriate molecular sieve candidate for C_3H_6/C_3H_8 separations [31, 32]. The ZIF-8 containing MMMs, which were also named PZ8-10 for 6FDA-DAM/ZIF-8 (90/10 wt/wt) and PZ8-20 for 6FDA-DAM/ZIF-8 (80/20 wt/wt), were fabricated by the same process as the one for PI/ZIF-67 MMMs and their gas permeation measurements were performed at the same conditions. The permeation results of our ZIF-8 containing MMMs were very close to those of ZIF-8 containing MMMs demonstrated by Zhang et al. [13] (Fig. S5). As shown in Fig. S5, the PZ67 MMMs exhibited a significant improvement in C_3H_6/C_3H_8 selectivity compared to PZ8 MMMs, but rather lower C_3H_6 permeability. Especially, the C_3H_6/C_3H_8 permselectivity of PZ67-20 which involves the actual ZIF-67 content of 21.1 wt% was comparable with that of

PZ8 MMMs containing the actual ZIF-8 content of 48.0 wt% by Zhang et al [13]. As indicated in Table S3, such difference was caused mainly by diffusivity selectivity rather than solubility selectivity. As discussed in the Section 4.1, the sorption capacities of ZIF-67 for both C₃H₆ and C₃H₈ gas molecules are almost identical, which is similar to ZIF-8 nanoparticles. The ZIF-67 containing MMMs, however, exhibited 25 ~ 32 % greater diffusivity selectivity than ZIF-8 containing analogs due to the enhanced molecular sieving behavior of ZIF-67 (Table S3).

Table 1. Single gas C₃H₆/C₃H₈ separation results of PI, ZIF-8 and ZIF-67 containing MMMs at 35 °C.

Sample	Permeability (Barrer)		Permselectivity
	C ₃ H ₆	C ₃ H ₈	C ₃ H ₆ /C ₃ H ₈
PI	16.63 ± 0.14	1.47 ± 0.05	11.3 ± 0.3
PZ67-10	24.52 ± 0.11	1.25 ± 0.02	19.6 ± 0.2
PZ67-20	34.14 ± 0.04	1.14 ± 0.01	29.9 ± 0.2
PZ8-10	26.10 ± 0.03	1.60 ± 0.03	16.3 ± 0.3
PZ8-20	37.73 ± 0.56	1.82 ± 0.06	20.7 ± 0.4

The intrinsic C₃H₆/C₃H₈ separation performances of ZIF-67 and ZIF-8 were predicted from our single gas permeation results by using the Maxwell model [13] and are represented in Table S4. The validity of Maxwell model-based C₃H₆ and C₃H₈ permeabilities of ZIFs was verified by confirming that our predicted permeation results for ZIF-8 are almost identical with those for ZIF-8 by Zhang et al. [13] (See Table S4). It should be noted that the direct comparison of the predicted separation performance of ZIF-8 with the experimental counterpart

from neat polycrystalline ZIF membranes is far-fetched due to the difficulty of controlling grain boundaries of polycrystalline ZIF membranes. The intrinsic C_3H_6 permeability and C_3H_6/C_3H_8 selectivity of ZIF-67 are 150.7 Barrer and 251, respectively (vs. C_3H_6 permeability of 275.6 Barrer and C_3H_6/C_3H_8 selectivity of 125 for ZIF-8) (Fig. 3). ZIF-67 provided 45% lower C_3H_6 permeability, but 100% higher C_3H_6/C_3H_8 permselectivity than ZIF-8, thereby affecting the tendency of C_3H_6/C_3H_8 separation performance for the respective MMMs. As Kwon et al. demonstrated based on FT-IR spectra[15], the coordination bonding between cobalt and nitrogen in ZIF-67 is stiffer than that between zinc and nitrogen in ZIF-8, consequently leading to the more restricted flipping motion of 2-mIM organic ligands and thereby the reduction in the effective aperture size. This results in improved discrimination between C_3H_6 and C_3H_8 penetrants while leading to reduced permeabilities of C_3H_6 and C_3H_8 . It is noteworthy that improving C_3H_6/C_3H_8 selectivity of polymer membranes is challenging due to their similar molecular size as well as condensable properties [33].

Fig. 3. Single gas C_3H_6/C_3H_8 separation performances of PI and MMMs and the predictions for MMMs and ZIFs with the upper bound curve [4].

Furthermore, the mixed gas permeation measurements were performed for PI and ZIF-67 containing MMMs by using a binary gas mixture of C_3H_6/C_3H_8 (50/50 mol/mol) at C_3H_6 partial pressure of 2 atm and 35 °C with the mixed gas separation performance for PI/ZIF-8 MMMs from Zhang et al's work [13] for reference (Fig. 4). As represented in Fig. 4, the mixed gas separation performance was depreciated compared to the corresponding single gas counterpart due to the competition effect between two gas molecules as well as C_3H_6 -induced bulk effect. The strong negative sorption coupling effects between C_3H_6 and C_3H_8 owing to the similarity of their condensabilities may diminish C_3H_6 permeability and C_3H_6/C_3H_8 separation factor [34]. Also, the high permeability of C_3H_6 for PI and ZIF-67 containing MMMs induces a bulk effect, which accelerates movement of larger gas molecules (C_3H_8) by being carried by smaller gas molecules (C_3H_6), abating the separation factors in mixed gas conditions [35]. Nevertheless, it should be noted that a high separation factor can be still realized at a practical concentration level (i.e., 20 wt%) of molecular sieves by utilizing ZIF-67 nanoparticles.

Fig. 4. C_3H_6/C_3H_8 separation performances of PI and PI-based MMMs under single as well as mixed gas conditions. Note: the data of PZ8 were taken from the Zhang et al's work [13] for

comparison and the numbers next to the symbols of MMMs represent the actual weight fractions of ZIFs.

4.3.2 Temperature-dependent characteristics of gas transports

Temperature dependence of C_3H_6/C_3H_8 separation performance was evaluated by characterizing transport behaviors at three different temperatures of 35, 50, and 70 °C in order to further investigate the molecular sieving behavior of ZIF-67 and ZIF-8 nanoparticles in MMMs. Both C_3H_6 and C_3H_8 permeabilities of all samples (i.e., PI, PZ67-20, and PZ8-20) were gradually enhanced with increasing operating temperature (Fig. 5a). The activation energy for permeation is decided by the combination of two competitive components: the activation energy of diffusion (positive) and the heat of sorption (negative) (See Equation (11)). Axiomatically, the permeability augmentation with increasing temperature indicated that the diffusivity is a more dominant contributor than the solubility for all three samples. Also, Fig. 5b exhibits that the C_3H_6/C_3H_8 selectivity decreased continually for all samples with increasing temperature, since the larger penetrant, C_3H_8 , has higher diffusional activation energy than the smaller penetrant, C_3H_6 (Table 2).

Overall, the permeation activation energy of C_3H_6 decreased while that of C_3H_8 increased with the addition of molecular sieves (ZIF-67 and ZIF-8 nanoparticles) compared to that of respective penetrant in PI. Comparing with the activation energy of permeation for PI, the extent of reduction in the activation energy of permeation of C_3H_6 for PZ67-20 was less than that for PZ8-20, but the extent of increase in the permeation activation energy of C_3H_8 was greater for PZ67-20 than that for PZ8-20, which is consistent with our single gas permeation results (See Fig. 3). These contrasting changes in the activation energy for

permeation through PZ67-20 and PZ8-20 are construed in terms of diffusivity and solubility for each MMM. The diffusional activation energies of C_3H_6 for both PZ67-20 and PZ8-20 decreased compared to that for PI due to the free diffusion of C_3H_6 through the large cages of the molecular sieves. Interestingly, the diffusional activation energy of C_3H_8 through PZ8-20 still decreased compared to that for PI while that through PZ67-20 rather increased. This observation strongly supports that ZIF-67 performs better for the C_3H_6/C_3H_8 separation based on molecular sieving principle than ZIF-8, even though both PZ67-20 and PZ8-20 substantially increased the absolute values of $\Delta E_{D, C_3H_6, C_3H_8}$ (i.e., $|E_{D, C_3H_6} - E_{D, C_3H_8}|$) as compared to PI. The heat of sorption of the MMMs (PZ67-20 and PZ8-20) also exhibits different trends depending on the molecular sieves (Table 2). In general, the sorption process of a gas in a polymer involves an exothermic process and the more negative the heat of sorption, the stronger the interactions between the gas and the polymer. Both PI and PZ8-20 show a negative value of $\Delta H_{S, C_3H_6, C_3H_8}$ (i.e., $H_{S, C_3H_6} - H_{S, C_3H_8}$), implying that the sorption of C_3H_6 is more favorable than that of C_3H_8 in both PZ8-20 and PI. The PZ67-20, however, exhibits a positive value of $\Delta H_{S, C_3H_6, C_3H_8}$, indicating a more favorable sorption of C_3H_8 than C_3H_6 in PZ67-20, which may consequentially make it difficult for C_3H_8 to desorb from the sorption site on diffusional jump.

Fig. 5. Temperature dependence of permeability (a) and permselectivity (b) for PI (triangle), PZ67-20 (circle), and PZ8-20 (square) at 2 atm.

Table 2. Activation energies for permeation (E_P) and diffusion (E_D) and heats of sorption (H_S) for PI and MMMs.

Sample	Gas	E_P (kJ/mol)	E_D (kJ/mol)	H_S (kJ/mol)
PI	C_3H_6	7.3	20.4	-13.1
	C_3H_8	12.2	24.4	-12.2

PZ67-20	C ₃ H ₆	4.9	16.8	-11.9
	C ₃ H ₈	16.7	31.6	-14.9
PZ8-20	C ₃ H ₆	2.4	11.6	-9.2
	C ₃ H ₈	14.2	22.4	-8.2

4.3.3 Energetic selectivity vs. entropic selectivity

For C₃H₆/C₃H₈ separation, hitherto, ZIF-67 and ZIF-8 nanoparticles in MMMs showed the different extents of molecular sieving effects, which strongly affect the diffusivity selectivity of MMMs. Diffusivity selectivity can be separated into the energetic selectivity associated with the size of gas penetrants and membrane pores and the entropic selectivity associated with the shape of gas penetrants and membrane pores [36]. There have been a few studies considering the energetic and entropic selectivity of polymeric membranes for gas separations and most of them are focused on O₂/N₂ separations. Especially, the Koros group intensively studied energetic and entropic contributions to the diffusivity selectivity of O₂/N₂ separations for several 6FDA-based polyimide membranes [37]. They concluded that the entropic selectivity of those polymers is negligible or favorable to N₂ than O₂ (i.e., the entropic selectivity of polymeric membranes for O₂/N₂ separations was less than unity). Nevertheless, the diffusivity selectivity of most 6FDA-based polyimides in their work was greater than 4 due to the high energetic selectivity. The relatively large size of N₂ requires more activation energy than O₂ for diffusional jump which restricts its movements through locally ordered chain segments [37]. Although we confirmed that the 6FDA-DAM exhibits the O₂/N₂ entropic selectivity less than unity (Table S5), the entropic contribution for C₃H₆/C₃H₈ separations was 2.1 (Table 3) which is probably associated with the nature of polyatomic molecules.

Previous research demonstrated that a high separation performance of inorganic molecular sieves including zeolite 4A or carbon molecular sieve (CMS) membranes results from a considerable contribution of entropic selectivity [33, 36, 38]. Unlike CMS membranes possessing slit-like rigid pore structures, the high C₃H₆/C₃H₈ separation performances of both PZ8-20 and PZ67-20 were realized by a substantial enhancement of energetic selectivity (Table 3). ZIFs in MMMs significantly improved the energetic selectivity with sacrificing entropic selectivity in increasing diffusivity selectivity for C₃H₆/C₃H₈ separations, which may be attributed to the well-defined cylinder-like pore structures of the ZIFs by the six membered rings. Such high energetic contribution to diffusivity selectivity of ZIF-containing MMMs was consistent with the results from polycrystalline ZIF-8 membranes; the ZIF-8 membranes with C₃H₆/C₃H₈ diffusivity selectivity of 125 showed an extremely high energetic selectivity of 1.3E+11 and a low entropic selectivity of 1.0E-10 [39]. Moreover, the energetic selectivity of C₃H₆/C₃H₈ for PZ67-20 was 375% greater than that for PZ8-20, while the entropic selectivity of C₃H₆/C₃H₈ for PZ67-20 was 71 % less than that for PZ8-20 (Table 3). A significant improvement in the energetic selectivity of C₃H₆/C₃H₈ for PZ67-20 results in higher C₃H₆/C₃H₈ diffusivity selectivity compared to PZ8-20 albeit lower C₃H₆/C₃H₈ entropic selectivity.

Table 3. The energetic, entropic, and diffusivity selectivity for C₃H₆/C₃H₈ separations in PI, PZ67-20 and PZ8-20.

Sample	Energetic Selectivity	Entropic Selectivity	Diffusivity Selectivity
PI	4.8 ± 0.002	2.1 ± 0.01	10.1 ± 0.1
PZ67-20	322.7 ± 0.4	0.08 ± 0.0001	24.8 ± 0.2
PZ8-20	67.8 ± 0.3	0.28 ± 0.001	18.7 ± 0.2

The higher C_3H_6/C_3H_8 energetic selectivity of PZ67-20 over PZ8-20 is attributed to the efficient size sieving effect of ZIF-67. When gas penetrants execute diffusional jumps from a normal state to another normal state, they have to pass through the activated state by overcoming the repulsion energy as well as the desorption energy [40]. In molecular sieving media such as ZIF-67, the normal state indicates the sorbed gas molecules within their large cavities, while the activated state corresponds to the gas molecules passing through constricted passages between large cavities [37]. Although both ZIF-67 and ZIF-8 involve the same organic ligand, 2-mIM, the higher electronegativity of cobalt in ZIF-67 than that of zinc in ZIF-8 induces stiffer ionic bond with nitrogen in 2-mIM, possibly restricting the flipping motion of organic ligands [15, 16]. Consequentially, the more restricted flipping motion increased the efficiency of molecular sieving effect of ZIF-67 comparing with that of ZIF-8, requiring more repulsion energy for the diffusional jump of C_3H_8 . Also, the more negative heat of sorption of C_3H_8 than that of C_3H_6 in ZIF-67 (Table 2) corresponds to more desorption energy of C_3H_8 , contributing to increase in the energetic selectivity of C_3H_6/C_3H_8 .

Although the smaller entropic selectivity of PZ67-20 than PI is counter-intuitive (Table 3), this can be explained by applying the transition state theory (TST) to C_3H_6/C_3H_8 transport behaviors in ZIF-67. Based on the TST, the entropic selectivity can be estimated by dividing the ratio of partition functions of the fast gas for the activated and normal states by that for the slow gas (Equation S2) [36]. The partition function is the product of the translational, vibrational, and rotational partition functions (Equation S3). It should be noted that the vibrational partition functions can be simply withdrawn for the consideration of entropic selectivity in TST due to the unrestricted movements of gas molecules in both normal and activated states [36]. The partition functions for polyatomic gas molecules such as C_3H_6 and

C₃H₈ were calculated by using the Equations S4, S5, and S6 represented in Supporting Information (Table S6).

As shown in Fig. 6, both C₃H₆ and C₃H₈ are simplified as cuboids with the corresponding dimensions [33]. In order for both C₃H₆ or C₃H₈ to penetrate through ZIF-67, the minimally required aperture size of ZIF-67 could be conjectured to be at least 4.5 Å based on their cuboid dimensions (Fig. 6). Nevertheless, it should be noted that the effective pore size of ZIF-67 could be smaller than 4.5 Å. Also, the penetrants slightly larger than 4.5 Å might be still accessible to ZIF-67, due to the flexible characteristics of 2-mIM in ZIF-67 [41]. The large cavities of ZIF-67 where gas molecules stay at the normal state were presumed to have the same size as those of ZIF-8 (i.e., 12.5 Å) [39], since the sorption capacity of ZIF-67 was analogous to that of ZIF-8 as discussed in the section 4.1. In these regards, both C₃H₆ and C₃H₈ penetrants in the large cavities of ZIF-67 can freely translate into x, y, and z directions coupled with all the possible rotations; both C₃H₆ and C₃H₈ penetrants have 3 translational modes as well as 3 rotational modes at the normal state of ZIF-67 as depicted in Fig. 5. When those gas molecules, however, are in the activated state, the translation of C₃H₈ would be allowed to the directions of y and z within a very limited space of 0.2 Å, which is the difference between the presumed window size of ZIF-67 (4.5 Å) and the cross-sectional dimensions of C₃H₈ (4.3 Å), while the translation of C₃H₆ would be possible only for y direction (Fig. 5). Interestingly, although C₃H₈ exhibited one more translational degree of freedom compared to C₃H₆ at the activated state, the translational entropic selectivity of C₃H₆/C₃H₈ for ZIF-67 was close to 2 (Table S6). It is because the y-directional translational movements of planar C₃H₆ might be more mobile than the movements of bulky C₃H₈. The significantly declined entropic selectivity of PZ67-20 was mainly ascribed to the considerable rotational limitation of C₃H₆ compared to

C_3H_8 in the activated state of ZIF-67, albeit the impeded rotations in the direction of y and z for both penetrants in the activated state. While C_3H_8 gas molecules were able to rotate along the x axis in the activated state, the vertical rotation of C_3H_6 was very limited, since the height of C_3H_6 of 4.5 Å was admittedly stuck in the expected minimum window size (i.e., 4.5 Å) of ZIF-67. The low entropic selectivity of C_3H_6/C_3H_8 (i.e., 0.08) for ZIF-67 essentially resulted from the remarkably low rotational entropic selectivity of 0.04 (Table S6).

Fig. 6. Illustration of translational and rotational degree of freedom in the normal and activated state for C_3H_6 and C_3H_8 in passing through ZIF-67.

4.3.4 Physical stability of ZIF-67 containing MMMs

Substantial reduction in the permeability of glassy polymeric membranes over time, *so-called* physical aging, is a critical drawback for their gas separation applications. It is, therefore, of great interest to arrest their physical aging. In general, this physical aging is more

critical for glassy polymers with high fractional free volume (*FFV*) since their non-equilibrium excessive free volume tends to become equilibrium states via the time-dependent chain relaxation process or densification [42].

The C₃H₆ permeability variations for both PI and PZ67-20 were monitored up to 75 days at 35 °C and 2 atm while the thickness of the membranes was maintained similar (i.e., 10 ± 1 μm) in order to eliminate any thickness-induced complication [42-44]. As shown in Fig. 7a, the permeability of C₃H₆ for PI substantially decreased in the early stage, especially within 10 days, and reached 3.82 Barrer in 75 days, which is only 25 % of the initial permeability. Changes in C₃H₆ permeability for PZ67-20 were, however, relatively marginal over time. A closer analysis reflects that a substantial reduction in the C₃H₆ permeability for PI can be attributed likely to the substantial reduction in the C₃H₆ diffusivity. On the contrary, the PZ67-20 exhibits gradual, but still marginal reduction in both C₃H₆ diffusivity and C₃H₆ solubility (Fig. 7b and c).

Fig. 7. Normalized permeability (a), diffusivity (b), and solubility (c) of C_3H_6 for PI and PZ67-20 at 35 °C as a function of time.

To further investigate the reduced physical aging rate of ZIF-67 containing MMMs compared to PI, the dual-mode model parameters of C_3H_6 and C_3H_8 for pristine and aged PI

and PZ67-20 were obtained by fitting the experimental sorption isotherm data represented in Fig. 8 (Table 4). The Langmuir affinity constant, b values of C_3H_6 and C_3H_8 for both PI and PZ67-20 remain almost constant over the test period and also the slight deviations are still within error ranges considering that all samples were still being aged during characterization. Langmuir affinity constant of a specific gas depends on the chemical structure and therefore, it is not expected to change over time as long as the chemical structure is conserved. The PI, however, exhibits severe reduction in Henry's law constant, k_D and Langmuir sorption capacity, C_H' for both C_3H_6 and C_3H_8 over time, while the PZ67-20 shows trivial reduction in those parameters despite the fact that the actual percentage of polymer in PZ67-20 is substantially lower (i.e., 78.9 wt% and 64.9 vol%) compared to neat polymer matrix. The parameters, k_D and C_H' , have to do with the densely packed equilibrium regions and the non-equilibrium microvoids in polymer, respectively [45]. The trivial reduction in these parameters implies that the shrinkage of overall free volumes of PI was definitely hampered by the presence of ZIF-67 nanoparticles.

Fig. 8. Sorption isotherms of C_3H_6 (a) and C_3H_8 (b) at 35 °C for PI and PZ67-20 before vs. after aging of 30 days.

Table 4. Dual-mode model parameters for C_3H_6 and C_3H_8 in PI and PZ67-20 at 35 °C.

Sample	Aging (days)	Gas	k_D ($cm^3(STP)/$ $cm^3(poly)/psia$)	C_H' ($cm^3(STP)/$ $cm^3(poly)$)	b (1/psia)
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PI	-	C ₃ H ₆	0.39 ± 0.02	24.11 ± 0.79	0.51 ± 0.07
		C ₃ H ₈	0.37 ± 0.03	22.46 ± 1.03	0.57 ± 0.08
	30	C ₃ H ₆	0.28 ± 0.03	18.20 ± 0.85	0.57 ± 0.09
		C ₃ H ₈	0.22 ± 0.03	17.47 ± 1.00	0.38 ± 0.06
PZ67-20	-	C ₃ H ₆	0.58 ± 0.06	53.76 ± 2.28	0.32 ± 0.03
		C ₃ H ₈	0.44 ± 0.03	46.80 ± 1.08	0.41 ± 0.02
	30	C ₃ H ₆	0.45 ± 0.06	50.92 ± 2.10	0.30 ± 0.03
		C ₃ H ₈	0.41 ± 0.02	44.65 ± 0.60	0.38 ± 0.01

Interestingly, there was a similar observation with our results for the deceleration of physical aging rates induced by the introduction of nanoparticles, polyhedral oligomeric silsesquioxane (POSS), in poly(1-(trimethylsilyl)-1-propyne) (PTMSP) [46]. The permeability of PTMSP, well-known for a high permeability due to its high free volume, severely decreased over time even after crosslinking. However, the PTMSP containing 10 wt% POSS showed the significantly improved the physical aging resistance by occupying some of the large free volume elements, despite the permeability loss due to the impermeable characteristic of POSS [46]. The embedded nanoparticles in polymer matrix can play a role of buttress between polymeric chains, preventing decrease in free volume (Fig. 9a and b). More specifically, ZIF-67 nanoparticles rigidify polymer chains of the large free volume elements of PI around them through hydrophobic nature-induced strong affinity, verified by increase in T_g (Fig. S3), retarding their rapid relaxation. Such beneficial anti-aging effect by nanoparticles, however, might be infeasible in the absence of a good adhesion between nanoparticles and polymer (Fig. 9c) since the polymer chains still have enough freedom to be relaxed. It should be noted that

the PZ8-20 also showed the same physical stability as PZ67-20 did (Fig. S6). Such beneficial features of mitigating permeability reduction over time assure a potential application of ZIF-67 containing MMMs for gas separations.

Fig. 9. Schematic of free volume changes of polymer by physical aging for PI (a), ZIF-67 containing MMMs with strong adhesion (b), and ZIF-67 containing MMMs with weak adhesion (c).

5. Conclusions

A new promising molecular sieve, ZIF-67, for C_3H_6/C_3H_8 separations was successfully incorporated into 6FDA-DAM polymer matrix with a good dispersion as well as good adhesion with polymer matrix. 6FDA-DAM/ZIF-67 (80/20 wt/wt) MMMs (i.e., PZ67-20) involving a practically feasible ZIF-67 content level of 21.1 wt% achieved a C_3H_6/C_3H_8 separation factor of 19 under the equimolar binary mixture conditions at 35 °C. Temperature-dependent transport studies enabled thorough investigation on the molecular sieving behavior of ZIF-67

nanoparticles in MMMs. The higher C_3H_6/C_3H_8 selectivity of PZ67-20 MMMs over that of PZ8-20 counterparts was attributed to a higher diffusivity selectivity induced by a combination of much higher repulsion energy and more negative heat of sorption for C_3H_8 penetrants in ZIF-67. Also, the high C_3H_6/C_3H_8 diffusivity selectivity of PZ67-20 MMMs was achieved by a significantly high energetic selectivity despite loss in the entropic selectivity. A loss in the C_3H_6/C_3H_8 entropic selectivity of PZ67-20 compared to that of PI was successfully demonstrated by using the transition state theory. The Maxwell model was used to estimate the intrinsic separation performance of ZIF-67, showing a C_3H_6 permeability of 150.7 Barrer, which is 45% less than that of ZIF-8, but a C_3H_6/C_3H_8 selectivity of 251, which is 100% higher than that of ZIF-8. In the light of the fact that both C_3H_6 and C_3H_8 are similarly sized as well as condensable, ZIF-67 can be a promising replacement for ZIF-8 molecular sieves for C_3H_6/C_3H_8 separations. In addition to the excellent separation performance of ZIF-67 containing MMMs, the membranes showed substantially improved physical aging resistance due to a buttress role of ZIF-67 between polymer chains in the large free volume elements, further supporting their practical application for C_3H_6/C_3H_8 separations.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org>.

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Graphical Abstract