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Sub-Zero Temperature Synthesis of Pressure-Resistant ZIF-8 Membrane with Superior C₃H₆/ C₃H₈ Separation Performance

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and twin zinc source. Benefiting from the precisely tuned nucleation and growth kinetics, both the grain boundary structure and thickness of prepared ZIF-8 membrane could be well controlled, resulting in stable C_3H_6/C_3H_8 selectivity approaching 167 irrespective of operation pressure and C_3H_6 feed fraction with steady C_3H_6 permeance up to 3.2×10^{-8} mol m⁻² s⁻¹ Pa⁻¹, which ranks the highest among all porous α -Al₂O₃-supported ZIF-8 membranes reported in literature. In addition, the above protocol is featured

ZnO buffer layer ZIF-8 membrane

with high reproducibility, which is of vital importance for the scale-up manufacture. Our research provides a promising solution to remaining concerns hindering large-scale production and application of ZIF-8 membranes toward reliable separation of C_3H_6/C_3H_8 gas mixture.

D eveloping an innovative energy-efficient olefin/ paraffin (e.g., C_3H_6/C_3H_8) separation technology represents an inherent requirement in the petroleum refining industry.¹⁻⁴ In comparison with the dominant energyintensive cryogenic distillation C_3H_6/C_3H_8 separation process, which accounts for nearly 0.3% of global energy consumption,^{5,6} membrane-based separation as an alternative to conventional separation technologies possesses tremendous superiority in terms of energy conservation, capital cost reduction, environmental protection, and small footprint.⁷⁻¹⁰

Among various C_3H_6 -selective membrane materials, zeolitic imidazolate framework-8 (ZIF-8), which is assembled from zinc ions (Zn²⁺) coordinated with 2-methylimidazole (2-mIm) ligands (Figure S1a),¹¹ has been extensively studied and widely recognized as the best-performing membrane candidate for the precise separation of C_3H_6/C_3H_8 gas mixture due to an appropriate pore-aperture size (~4.0 to 4.2 Å, Figure S1b) enabling accurate discrimination of the subtle difference in kinetic diameters of C_3H_6 (~4.0 Å) and C_3H_8 (~4.2 Å),^{12,13} thereby easily transcending the tradeoff between permeability and selectivity commonly encountered in polymer membranes and mixed-matrix membranes (MMMs).¹⁴ Numerous efforts have been devoted to the fabrication of ZIF-8 membranes with commercially competitive C_3H_6/C_3H_8 separation performances. Diverse synthetic protocols, including in situ synthesis, epitaxial synthesis, contra-diffusion synthesis, interfacial microfluidic processing, current-driven synthesis, all-vapor phase processing, semisolid processing, and supercritical fluid processing, have been developed for commercial production of ZIF-8 membranes for high-purity C_3H_6 production.^{15–24} To date, overall C_3H_6/C_3H_8 separation performances of ZIF-8 membranes had outperformed those of other membrane materials (e.g., polymer, MMMs, zeolite, and carbon-based membranes).^{25–28} Despite the above achievements, there are still several obstacles that must be overcome before delving into industrial applications. On the one hand, reproducible preparation of high-quality ZIF-8 membranes was an essential prerequisite for their large-scale production; on the

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other hand, stable separation capability under practical operation conditions, including varying pressures, temperatures, and C_3H_6 feed ratios, was the prerequisite for industrial applications.^{10,29}

For the synthesis of C₃H₆-permselective ZIF-8 membranes, water has been recognized as an ideal solvent due to its strong deprotonation ability.^{30,31} Unfortunately, ZIF-8 nucleation and growth in the bulk solution proceed very fast even at room temperature (RT), causing the loss of kinetic control over the ZIF-8 membrane formation. As a result, it becomes very difficult to precisely tune the microstructure (e.g., grain boundary defects, thickness, and uniformity) and therefore the separation performance of prepared ZIF-8 membrane.^{32,33} For instance, grain boundary defects (i.e., nonselective intercrystalline pathway) in ZIF-8 membrane not only reduce C_3H_6/C_3H_8 selectivity but also may cause severe performance deterioration under elevated pressure; $^{33-35}$ excessive thickness may lead to lower C3H6 permeance, while a low degree of microstructure uniformity among ZIF-8 membranes may give rise to poor performance reproducibility. Alternatively, reducing the reaction temperature enables effective retardation of ZIF-8 nucleation and growth in the bulk solution, which is advantageous for exerting precise control over the kinetics of membrane formation and therefore final microstructure of ZIF-8 membranes. At present, ZIF-8 membranes have been prepared by restrained secondary growth at temperatures as low as 8 °C, resulting in reduced thickness as well as lower crystallinity. Nonetheless, the separation factor (SF) of $C_3H_6/$ C_3H_8 gas mixture remained unsatisfactory (~40), which might be attributed to relatively slow diffusion rates of Zn²⁺ ions and 2-mIm ligands in the bulk solution upon approaching the freezing point of water, thereby leading to a poor grain intergrowth.36

Herein, we achieved the fabrication of ZIF-8 membranes with superior C_3H_6/C_3H_8 separation performance by carrying out in situ growth at sub-zero temperature, which was intrinsically beneficial for maintaining a high degree of microstructure uniformity (i.e., high reproducibility) and low thickness (i.e., high C_3H_6 permeance). To warrant a liquid-state reaction even below the freezing point, in this study, a methanol–water binary mixture was used as the reaction medium instead of pure water.

We initially attempted to prepare ZIF-8 nanocrystals with the above binary solvent at -5 °C. Our experimental results indicated that in comparison with ZIF-8 crystals synthesized at RT, the crystal size was remarkably reduced (~50 nm) with no compromise in the size uniformity (Figure S2). Moreover, such morphology could be obtained at relatively wide time range (Figure S3), which was advantageous to improve reproducibility.

Subsequently, spin-coating technique was employed to deposit ZIF-8 seed layer for sub-zero temperature epitaxial growth. After deposition under optimized conditions, the substrate surface had been fully and uniformly covered with a 150 nm-thick seed layer (Figure S4). After epitaxial growth at -5 °C for 24 h, a well-intergrown ZIF-8 membrane with thickness of ~ 200 nm and grain size of ~ 250 nm had been formed (Figure S5a-c). Relevant XRD pattern implied that prepared ZIF-8 membrane remained randomly oriented (Figure S5d). Gas permeation results indicated that H₂ and C₃H₆ permeances reached 1.37 × 10⁻⁶ mol m⁻² s⁻¹ Pa⁻¹ and 7.06 × 10⁻⁸ mol m⁻² s⁻¹ Pa⁻¹, respectively, which were close to the values obtained on the bare α -Al₂O₃ substrate, thereby

implying a negligible diffusion barrier. Nevertheless, its idea H_2/C_3H_6 (19.34) and C_3H_6/C_3H_8 (8.61) selectivity remained fairly low in comparison with other reported ZIF-8 membranes (Figure S5e,f),^{15–24} implying that there remained some grain boundary defects in the membrane, owing to insufficient driving force for the growth of ZIF-8 seeds. In addition, severe concentration polarization and reduced mobility of both Zn²⁺ and 2-mIm in the bulk solution at such a low temperature gave rise to insufficient nutrient supply at the solution–substrate interface and therefore poor intergrowth between adjacent ZIF-8 crystallites.

In response to the above issues, here, a ZnO buffer layer, which was obtained by calcination of sol-gel-derived precursor layer, was deposited on porous α -Al₂O₃ substrate to supplement Zn²⁺ ions required for the membrane growth (Figure S6a). After sub-zero temperature growth with "twin zinc source" under given conditions, that is, $Zn(OAc)_2$ in the bulk solution and ZnO buffer layer on the substrate surface, the thickness and grain size of prepared ZIF-8 membrane increased to 600 and 800 nm (Figure S6b-d), thereby leading to better intergrowth between adjacent ZIF-8 crystallites. Correspondingly, its ideal H_2/C_3H_6 (25.15) and C_3H_6/C_3H_8 (44.10) selectivity were significantly enhanced with only slight compromise in gas permeances (H₂ permeance, 1.03×10^{-6} mol m⁻² s⁻¹ Pa⁻¹; C₃H₆ permeance, 4.10×10^{-8} mol m⁻² s⁻¹ Pa^{-1}) (Figure S6e,f). Nonetheless, the C_3H_6/C_3H_8 selectivity remained lower than the theoretical value (~ 125) ,³⁷ possibly owing to uneven surface coverage and insufficient chemical activity of the ZnO buffer layer (Figure S7).

To address this issue, we proposed to combine the above two deposition processes to improve the microstructure uniformity and chemical activity of the ZnO buffer layer (shown in Figure 1). Initially, the ZIF-8 crystal layer and Zn-



Figure 1. Schematic illustration of sub-zero temperature synthesis of the ZIF-8 membrane.

based gel layer were sequentially spin-coated on the porous α -Al₂O₃ substrate (Figure 2a); subsequently, calcination was carried out to convert the above layers into a uniform and reactive ZnO buffer layer (Figures 2b and S8); in the next step, the above processes were repeated twice for better surface smoothness and uniformity control of the ZnO buffer layer (Figures S9–S11). Finally, sub-zero temperature growth was



Figure 2. SEM images of (a) ZIF-8 crystal layer, (b) ZnO buffer layer, (c) top and (d) cross-sectional views of prepared ZIF-8 membrane. (e) Corresponding cross-sectional EDXS mapping (Zn, green; Al, magenta). (f) XRD patterns of simulated ZIF-8, ZIF-8 crystal layer, ZnO buffer layer, and prepared ZIF-8 membrane.

carried out at -5 °C for 24 h to prepare the ZIF-8 membrane with more balanced microstructure.

The ZIF-8 membrane prepared via the above protocol was subjected to SEM characterization. It was observed that both thickness and grain size of prepared ZIF-8 membrane slightly increased to 620 and 850 nm, respectively (Figures 2c,d and S12). The growth rate (defined as the membrane thickness divided by the growth time) of sub-zero temperature synthesis was comparable with that of all-vapor phase and supercritical fluid processing, but much lower than that of traditional solution-based protocols (Table S1), which was conducive to more precise control the growth kinetics of ZIF-8 membranes so that a high degree of microstructure uniformity and excellent performance reproducibility could be achieved. The cross-sectional EDXS pattern (Figure 2e) indicated that although the ZIF-8 top layer partially penetrated into underlying substrate pores, the penetration depth was quite limited, which was beneficial to improve its mechanical stability with negligible influence on the gas permeance. Relevant XRD pattern confirmed that after the reaction, a majority of the ZnO buffer layer had been converted to the ZIF-8 membrane (Figure 2f).

Gas permeation properties of the ZIF-8 membrane were first evaluated in a Wicke–Kallenbach permeation cell (Figure S13a). Single gas permeation results demonstrated that the order of gas permeance through prepared ZIF-8 membrane followed the same sequence as the kinetic diameter of gas molecules. Of particular note, owing to the flexibility of ZIF-8 framework caused by the rotation of 2-mIm ligands,^{12,38} there existed a sharp permeance cut-off between C_3H_6 and C_3H_8



Figure 3. (a) Single-gas permeances of prepared ZIF-8 membrane under ambient conditions as a function of the molecular kinetic diameters; the inset shows the corresponding Knudsen selectivity and ideal selectivity of different gas pairs. (b) Detailed comparison of C_3H_6/C_3H_8 separation performance of prepared ZIF-8 membranes with previously reported ZIF-8 membranes and other types of membranes (circle - top half green, bottom half white, α -Al₂O₃ supported ZIF-8 membranes; pentagon - top half white, bottom half green: other types of substrate supported ZIF-8 membranes; the dashed line represented the upper bound for porous α -Al₂O₃-supported ZIF-8 membranes for C_3H_6/C_3H_8 separation). The binary C_3H_6/C_3H_8 separation performance of prepared ZIF-8 membrane as a function of (c) operation temperature, (d) feed pressure, and (e) C_3H_6 feed fraction. (f) Long-term stability of prepared ZIF-8 membrane for C_3H_6/C_3H_8 separation under different separation conditions.

To investigate the reproducibility of this protocol, the C_3H_6/C_3H_8 separation performances of ZIF-8 membranes prepared in parallel were measured sequentially under ambient conditions. Our test results suggested that all prepared ZIF-8 membranes displayed outstanding C_3H_6/C_3H_8 selectivity in the range of 124–167 with remarkable C_3H_6 permeances $(1.5-3.2 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1})$ (Table S2), thereby confirming very high batch-to-batch reproducibility.

The C_3H_6/C_3H_8 separation performance of the above ZIF-8 membranes was compared with the literature. The performance of our membranes not only easily exceeded that of other types of membranes (including polymer membranes, MMMs, zeolite membranes, and carbon-based membranes, shown in Table S3) but also was superior to most ZIF-8 membranes reported in the literature. Although several ZIF-8 membranes supported on other types of substrates showed higher $C_3H_6/$ C₃H₈ SF or C₃H₆ permeance, such as AAO-supported ZIF-8 membrane prepared by current-driven synthesis method with a C₃H₆/C₃H₈ SF up to 304 and PSF-supported ZIF-8 membrane fabricated by interface layer polarization induction with a C_3H_6 permeance over 6×10^{-7} mol m⁻² s⁻¹ Pa⁻¹,^{20,39} the overall C_3H_6/C_3H_8 separation performance of our ZIF-8 membranes ranked the highest among all porous α -Al₂O₃supported ZIF-8 membranes (Figure 3b and Table S4).

Aiming at practical applications, our ZIF-8 membrane was further subjected to C_3H_6/C_3H_8 separation at elevated operation temperature (up to 150 °C) and pressure (up to 7 bar). It was observed that the C_3H_6 permeance declined slightly as temperature increased; simultaneously, SF of $C_3H_6/$ C_3H_8 gas mixture gradually decreased (Figure 3c), which was attributed to gradually pronounced adsorption of C_3H_6 on ZIF-8, while C_3H_8 showed an opposite trend.³⁷ Even so, SF of C_3H_6/C_3H_8 gas mixture remained ~100 at 50 °C, which fully met relevant industrial demands.

Several previous studies indicated that SF of C_3H_6/C_3H_8 gas mixture would inevitably fluctuate under varying operation pressure, owing to the existence of grain boundary defects in ZIF-8 membrane or increased effective aperture size caused by framework distortion.^{33–35,40,41} On the contrary, our membrane exhibited a steady SF toward C_3H_6/C_3H_8 gas mixture even if the feed pressure raised to 7 bar as required by the industry, which could be ascribed to effective elimination of grain boundary defects or probably suppressed framework flexibility.^{42,43} It was particularly noted that, unlike previous reports,^{33,34} the C_3H_6/C_3H_8 separation performance of our ZIF-8 membrane could be fully recovered even if the feed pressure dropped quickly from 7 to 1 bar (Figures 3d and S14), which was indicative of exceptional operation stability.

In addition, the permeation test without sweep gas (i.e., undiluted permeate) was carried out at 7 bar to further evaluate their potential industrial application. It could be observed that, consistent with previous results,^{21,44,45} the C_3H_6/C_3H_8 separation performance decreased due to the concentration polarization caused by the enrichment of C_3H_6

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on the permeate side. Even so, SF of C_3H_6/C_3H_8 gas mixture remained as high as 95.8 with C_3H_6 permeance of 63.3×10^{-10} mol m⁻² s⁻¹ Pa⁻¹, which had fully met the criteria required for industrial application (Table S5).

Simultaneously, the effect of C3H6 feed fraction on the C_3H_6/C_3H_8 separation performance was investigated, considering the possibility of varying C_3H_6/C_3H_8 molar ratios in the olefin production process. Our experimental results revealed that irrespective of C_3H_6 feed fraction, both the C_3H_6 permeance and SF of C3H6/C3H8 gas mixture remained unchanged (Figure 3e), which was rarely observed in previous studies,^{23,24} thereby recommending them superb candidates for steady operation in multiple application scenarios in a wide range of C₃H₆ feed fractions. Finally, long-term operation stability of prepared ZIF-8 membrane was studied. As was convincingly shown in Figure 3f, our membrane exhibited stable separation performance for at least 6 days not only under ambient conditions but also at elevated operation temperature and pressure, which was quite advantageous for their reliable application in industry.

To verify whether the reaction temperature exerted any influence on the microstructure and separation performance of prepared ZIF-8 membrane, herein a series of ZIF-8 membranes were prepared in a temperature range of -25 to $150 \,^{\circ}$ C, and their C_3H_6/C_3H_8 separation results were summarized in Table 1. It was observed that starting from $-25 \,^{\circ}$ C, with increasing reaction temperature, both the C_3H_6 permeance and SF of C_3H_6/C_3H_8 gas mixture increased, reached the maximium values at $-5 \,^{\circ}$ C, and then decreased (Figure 4). However, corresponding SEM images showed steadily increased grain size and membrane thickness (Figures S15 and S16), which

Table 1. C_3H_6/C_3H_8 Separation Performances of ZIF-8 Membranes Synthesized at Different Temperatures

	$C_{3}H_{6}$ permeance (×10 ⁻¹⁰ mol m ⁻² s ⁻¹ Pa ⁻¹)		SF	
$T(^{\circ}C)$	value	relative error	value	relative error
-25	9.16	14.4%	42.7	23.3%
	6.99		66.2	
	9.37		70.5	
	9.92		76.9	
-15	71.4	31.3%	75.8	10.2%
	46.2		85.9	
	33.2		91.6	
	51.1		96.5	
-5	287.4	31.7%	106.4	14.4%
	303.6		116.8	
	201.3		132.5	
	145.4		147.8	
30	52.7	29.8%	114.6	10.7%
	28.1		128.1	
	35.1		132.2	
	31.4		148.6	
80	98.5	86.5%	1.22	160.1%
	23.4		2.09	
	105.1		16.6	
	6.85		108.2	
150	756.5	120.9%	1.10	89.1%
	2389.9		1.12	
	321.9		1.14	
	22.7		4.72	



Figure 4. Dependence of C_3H_6 permeance and C_3H_6/C_3H_8 separation factor of ZIF-8 membranes on the synthetic temperature.

were indicative of gradually densified grain boundary structure and therefore higher gas diffusion resistance. Simultaneously, as shown in the XRD patterns and FT-IR spectra (Figures S17 and S18), characteristic peaks derived from ZnO buffer layers steadily weakened (and eventually disappeared), implying that increasing reaction temperature was beneficial for improving the conversion rate of ZnO buffer layers, thereby partially contributing to increased membrane thickness and densified grain boundary structure.

On the basis of the above results, a plausible mechanism was put forward for a better understanding of structural evolution of ZIF-8 membranes with increasing temperature (shown in Figure S19). At temperature of -25 °C, excessively low growth rate resulted in insufficient ZIF-8 nucleation and growth and therefore poor intergrowth between adjacent ZIF-8 crystallites. In addition, the low reactivity at such a low reaction temperature gave rise to relatively low conversion rate of the ZnO buffer layer (nonporous hexagonal wurtzite phase). Accordingly, both the C_3H_6 permeance and SF of C_3H_6/C_3H_8 gas mixture were relatively low, although high reproducibility could be maintained due to well-controlled nucleation and growth kinetics of ZIF-8 at such a low temperature. When the temperature rose to -15 °C, not only the mobility of nutrients (i.e., Zn²⁺ ions and 2-mIm ligands) in the bulk solution were enhanced but also conversion rate of the ZnO buffer layer was increased, resulting in more sufficient supply of nutrients for the membrane growth so that both the C_3H_6 permeance and SF of C_3H_6/C_3H_8 gas mixture were increased. Further increasing the reaction temperature to -5 °C resulted in balanced intergrowth between adjacent ZIF-8 crystallites, appropriate membrane thickness, and quasi-full conversion of the ZnO buffer layer, which cooperatively contributed to concurrently increased C_3H_6 permeance and SF of C_3H_6/C_3H_8 gas mixture by an order of magnitude. However, further increasing the reaction temperature to 30 °C resulted in uncontrolled intergrowth between adjacent ZIF-8 crystallites and excessive membrane thickness, $^{46-50}$ thereby leading to a significant decline in the C₃H₆ permeance. Further elevation of the growth temperature to higher than 80 °C led to significant decline in not only C_3H_6/C_3H_8 separation performance but also reproducibility, which could be attributed to the loss of kinetic control over the ZIF-8 membrane formation under

such high reaction temperatures. Therefore, conducting in situ growth at reaction temperature of -5 °C ensured a precise balance between grain boundary structure and membrane thickness while simultaneously maintaining a high degree of microstructure uniformity, thereby resulting in superior C₃H₆/C₃H₈ separation performance, pressure-independent SF of C₃H₆/C₃H₈ gas mixture, and high reproducibility.

To sum up, in this study, the sub-zero temperature synthetic protocol was developed for in situ preparation of high-quality ZIF-8 membrane through combining with twin zinc sources (i.e., $Zn(OAc)_2$ in the bulk solution and the ZnO buffer layer). The precisely tuned nucleation and growth processes at subzero temperature warranted well-controlled grain boundary structure, membrane thickness, and microstructure uniformity. Prepared ZIF-8 membrane exhibited stable C_3H_6/C_3H_8 selectivity approaching 167 with high C₃H₆ permeance up to 3.2×10^{-8} mol m⁻² s⁻¹ Pa⁻¹, irrespective of the operation pressure and C₃H₆ feed fraction. Furthermore, high reproducibility could be achieved easily. It is anticipated that this subzero temperature synthetic protocol could serve as a reliable tool for reproducible preparation of diverse MOF membranes with unique microstructure features and performance superiorities.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmaterialslett.2c00119.

Detailed experimental procedures and instrument used; detailed characterization data of ZIF-8 crystal layer, ZnO buffer layer and ZIF-8 membranes; detailed C_3H_6/C_3H_8 separation performance of ZIF-8 membranes (PDF)

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

ZIF-8, zeolitic imidazolate framework-8; MMMs, mixed-matrix membranes; RT, room temperature; SF, separation factor

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