

Supercritical Ethane Processing of ZIF-8 Membranes towards Pressure-Resistant C₃H₆/C₃H₈ Separation

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Abstract: ZIF-8 membranes have shown great promise in industrial-scale C₃H₆/C₃H₈ separation. Nonetheless, sustainable preparation of pressure-resistant ZIF-8 membranes remains a grand challenge. In this study, we pioneered the use of supercritical ethane (scC₂H₆) as reaction medium for preparing pressure-resistant ZIF-8 membranes. Membrane growth in neutral organic environment was proven to have less disturbance to structure integrity compared with supercritical CO₂ (scCO₂). Gas permeation results indicated that obtained ZIF-8 membrane exhibited an ideal C₃H₆/C₃H₈ selectivity of 172.1 with C₃H₆ permeance of 5.9×10⁻⁹ mol·m⁻²·s⁻¹·Pa⁻¹. Of particular note, the membrane maintained stable C₃H₆/C₃H₈ selectivity of ~150 with C₃H₆ flux of ~1.6×10⁻³ mol·m⁻²·s⁻¹ at operation pressure of 6 bar, which was significantly different from ZIF-8 membranes obtained from scCO₂ reaction medium. Through combining with advantages of zero pollutant discharge and full ligand recovery, our protocol holds great promise in sustainable preparation of pressure-resistant ZIF-8 membranes towards practical application in high-purity C₃H₆ production.

Introduction

As the raw material of diverse high value-added chemical products, light olefins (e.g., C₂H₄ and C₃H₆) have a wide range of applications in petrochemical industry. At present, cryogenic distillation has been widely used to separate C₃H₆ from the C₃H₆/C₃H₈ mixture; however, this is an energy-intensive process due to close boiling points of C₃H₆ (−47.7 °C) and C₃H₈ (−42.1 °C), accounting for 0.3 % of global energy consumption.^[1] In contrast, membrane separa-

tion shows great potential in energy-efficient C₃H₆/C₃H₈ separation due to the omission of thermally driven phase transition and thermodynamic equilibrium.^[2] Zeolitic Imidazolate Framework-8 (ZIF-8), which consists of Zn²⁺ ions coordinated with 2-mIm ligands with crystallographic theoretical aperture size of 0.34 nm.^[3,4] Owing to the unique gate-opening effect originated from intrinsic framework flexibility, the diffusion coefficient of C₃H₆ is 125 times higher than that of C₃H₈ in ZIF-8 framework,^[4a,6b] thereby holding great promise in precise screening C₃H₆ from C₃H₈. Diverse synthetic protocols, including in situ growth,^[5] epitaxial growth,^[6] interfacial microfluidic processing,^[7] electrochemical synthesis,^[8] and vapor phase transition,^[9] have been developed for preparing ZIF-8 membranes with exceptional C₃H₆/C₃H₈ separation performances. For instance, Jeong and Kwon reported the preparation of well-intergrown ZIF-8 membranes through in situ counter-diffusion method.^[5d,e] The semi-interlocked microstructure endowed the membrane with not only superior C₃H₆/C₃H₈ separation performance but also excellent mechanical stability; in addition, the precursor solution could be easily recycled and reused.

At present, high production cost per unit membrane area represents a great challenge facing bath production of high-performance ZIF-8 membranes.^[10] Pressurization has therefore become indispensable to increase the permeation flux.^[11,12a] However, the C₃H₆/C₃H₈ selectivity of ZIF-8 membranes commonly fluctuates under varying pressure and feed composition, making it difficult to ensure the purity of obtained polymer-grade C₃H₆. It therefore becomes crucial for sustainable preparation of ZIF-8 membranes capable of maintaining high and stable separation performances under varying operation pressure and feed composition.

Supercritical fluid (SCF) represents a special fluid with both liquid-phase density and gas-phase diffusivity.^[12] Its physicochemical property is highly sensitive to temperature and pressure,^[13] enabling more precise regulation of nucleation and growth kinetics,^[14] and therefore, microstructure of ZIF-8 membranes.^[15] Recently, we pioneered SCF processing of ZIF-8 membranes under supercritical CO₂ (scCO₂) environment. Maintaining scCO₂ in gas-like region was found to be essential for preparing ZIF-8 membranes with optimized microstructure and superior C₃H₆/C₃H₈ separation performance;^[16] moreover, since both used SCF solvents and residual 2-mIm ligands could be facily and fully recovered by pressure relief, zero pollutant discharge and near 100 % reagent recovery could be realized.^[17]

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Supercritical ethane (scC_2H_6), which possesses milder critical points (4.87 MPa, 32.2 °C) than scCO_2 (7.38 MPa, 31.2 °C), has been widely used in extraction of high-value organic products due to its high affinity to organic phase.^[18a] Nonetheless, its potential use as solvent for MOF synthesis has not been fully explored yet. Considering its intrinsic compatibility with organic ligands as well as chemical inertness, it is anticipated that ZIF-8 nucleation and growth kinetics could be precisely regulated, resulting in elimination of grain boundary defects, which is beneficial for stabilizing the $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ selectivity even under varying operation pressure and feed composition; simultaneously, sustainability can be maintained in view of the simplicity for separating ligands from scC_2H_6 after venting.

In this study, we pioneered the use of scC_2H_6 as reaction medium for epitaxially preparing ZIF-8 membranes (Figure 1). Through precise control of ZIF-8 nucleation and growth kinetics during SCF processing, semi-confined ZIF-8 membranes with desired microstructure could be readily obtained; moreover, since physicochemical properties of C_2H_6 are highly compatible with organic ligands, non-selective intergranular gaps could be largely avoided to ensure the integrity of membrane structure. Gas permeation results revealed that obtained membrane exhibited not only excellent $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ separation performance but also stable $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ selectivity under varying operation pressure and feed composition; simultaneously, since C_2H_6 could be facily segregated from residual ligands by venting the vessel, zero pollutant discharge and full ligand recovery could be easily achieved.

Results and Discussion

Initially, we verified the feasibility of preparing ZIF-8 powders through scC_2H_6 processing. In this study, both 2-mIm ligands and ZnO powders (Figure 2a) serving as zinc source were placed in the reactor vessel (Figure S1), and supercritical reaction was carried out under varying conditions (e.g., at 6 MPa and 60 °C for 24 h). According to the pressure (P) and temperature (T) employed, the resulting

ZIF-8 powder was named ZIF-8_{P,T}. SEM results (Figure 2b–e) indicated that the morphology of obtained ZIF-8 powders was quite different. For instance, uniform 200 nm-sized ZIF-8 powders were synthesized at 6 MPa and 60 °C (ZIF-8_{6,60}) for 24 h, while ZIF-8 powders with size in the range of 1–1.5 μm could be obtained at 8 MPa and 80 °C (ZIF-8_{8,80}) for 48 h. Relevant EDXS spectrum indicated the formation of core-shell structure comprising ZnO core and ZIF-8 shell after scC_2H_6 processing (Figure 2f). XRD patterns indicated that ZIF-8 powders were readily formed, irrespective of reaction conditions (Figure 2g). Subsequently, TGA test was carried out to verify thermal stability of scC_2H_6 -synthesized ZIF-8 powders. The decomposition temperature of obtained ZIF-8 powders reached 400 °C (Figure 2h), while their final weight loss was found to be closely related with reaction conditions. The conversion rate (C_R) of ZnO was further evaluated based on Eq. (1) in Support Information. At reaction condition of 6 MPa and 60 °C for 24 h, the ZnO C_R was calculated to be 10.0 %, while it sharply increased to 81.8 % upon conducting reaction at 8 MPa and 80 °C for 48 h (Figure 2h and i). Incomplete conversion of ZnO precursor into ZIF-8 powders could be attributed to the blocking effect of dense outer ZIF-8 shell, which acted as “protective layer” to prevent ligands from further reacting with remaining ZnO core.^[19,9c] Obviously, elevated reaction temperature and pressure gave rise to higher ZIF-8 nucleation and growth rates, and therefore, improved ZnO C_R .

It should be noted that the growth rate of ZIF-8 crystals in scC_2H_6 reaction medium was obviously lower than in traditional solvents (Figure S2 and Table S1), the C_R of ZnO powders in scCO_2 medium was studied either. The C_R of ZnO powders in scC_2H_6 medium at 8 MPa and 80 °C for 24 h reached 29.6 %, which remained much lower than the C_R of ZnO powders in scCO_2 medium under identical reaction conditions ($C_R=95.2\%$). Owing to neutral nature of C_2H_6 as solvent, the crystallization rate of ZIF-8 in scC_2H_6 solution containing 2-mIm was slower than weak alkaline solvents such as methanol and DMF, resulting in lower deprotonation rate of ligands, and therefore, lower C_R of ZnO precursor. Slowing down ZIF-8 nucleation and growth

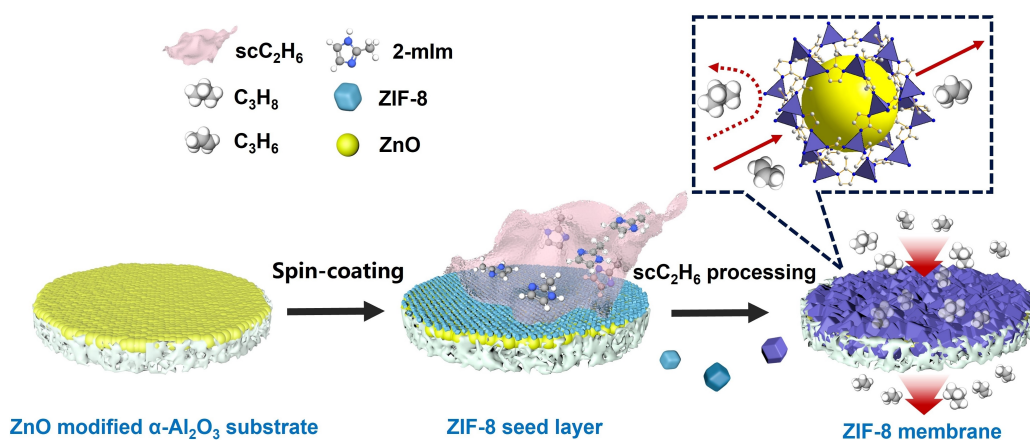


Figure 1. Schematic illustration of scC_2H_6 processing of ZIF-8 membranes.

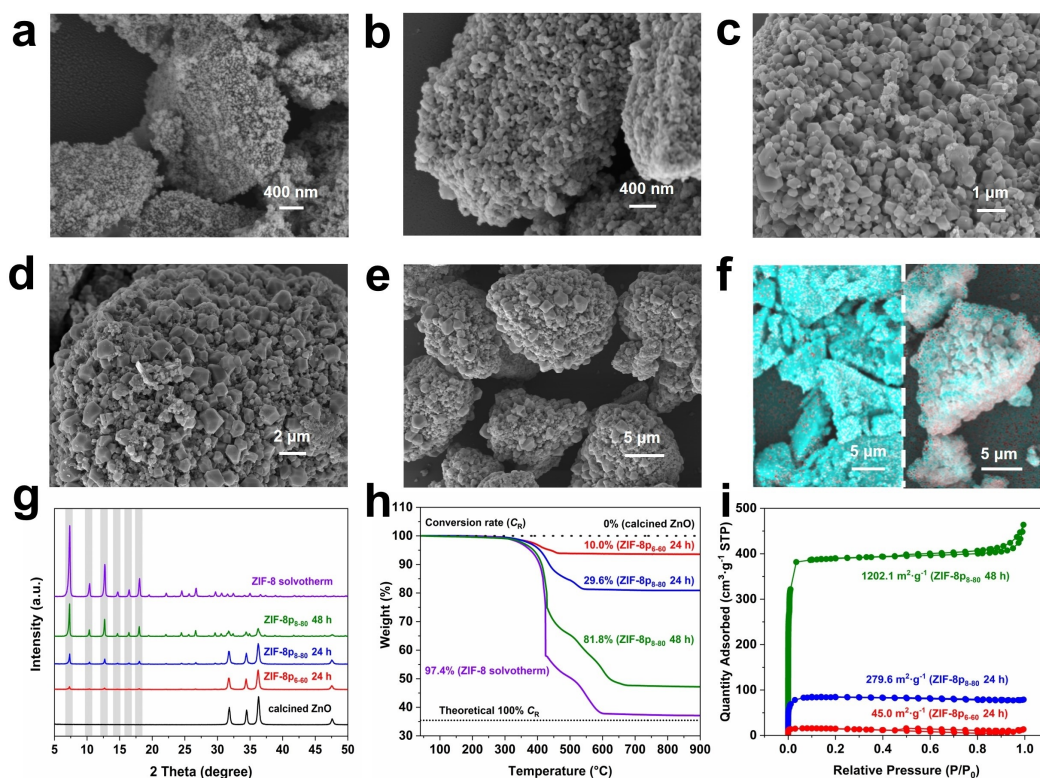


Figure 2. Characterization of ZIF-8 powders prepared via scC_2H_6 processing. (a) Calcined ZnO powder. ZnO@ZIF-8 nanospheres synthesized by scC_2H_6 under different conditions: (b) 6 MPa, 60°C, 24 h, (c) 8 MPa, 80°C, 24 h and (d, e) 8 MPa, 80°C, 48 h. (f) EDXS images of pure ZnO (Left) and ZnO@ZIF-8 (Right) structures. (Zn = blue, C = red). (g) XRD patterns and (h) TGA curves of corresponding powder. (i) N_2 adsorption-desorption curves of ZnO@ZIF-8 powders with different C_R .

rates are anticipated to exert more precise control over microstructure of ZIF-8 membranes.

The above results revealed that high-quality ZIF-8 membrane may be prepared through facile scC_2H_6 processing, which was briefly described as follow: Initially, according to our previous study,^[20] uniform Zn-based gel precursor layer was spin-coated on porous $\alpha\text{-Al}_2\text{O}_3$ substrate (Figure S3), followed by calcination for its conversion into uniform ZnO buffer layer (Figure 3a). Subsequently, the modified substrate was placed into a stainless-steel reactor containing 2-mM ligand powders. Finally, C_2H_6 was injected and supercritical reaction was allowed to carry out under given conditions.

We first tried employing in situ growth to prepare ZIF-8 membranes. Nonetheless, it turned out very difficult to prepare well-intergrown membranes with satisfying $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ separation performance. For instance, even under optimized reaction conditions of 6 MPa and 60°C, the $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ selectivity only reached 52.7 with C_3H_6 permeance of $1.1 \times 10^{-9} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$. This could be attributed to severe infiltration of Zn-based gel layer (Figure S4 and 5). Through combining with high mobility of scC_2H_6 , ZIF-8 layers appeared both on substrate surface and in substrate pores, thereby reducing C_3H_6 permeance; in addition, the nucleation bottleneck effect caused by low dissolution rate of ZnO buffer layer made it difficult to form well-intergrown ZIF-8 membrane due to insufficient nutrient supply.

To overcome the nucleation bottleneck effect, we expected that pre-deposition of a seed layer on substrate surface would promote the formation of well-intergrown ZIF-8 membrane via epitaxial supercritical growth; simultaneously, the presence of seed layer was beneficial for reducing membrane thickness due to the presence of sufficient nucleation sites. In this study, 70 nm-sized ZIF-8 seeds were prepared based on well-documented procedure (Figure S6), followed by repeated spin-coating on the ZnO buffer layer to obtain uniform 190 nm-thick seed layer (Figure 3b and c). Subsequently, supercritical reaction was conducted under scC_2H_6 environment.

Similar to the powder naming method, obtained ZIF-8 membrane was named with ZIF-8 $\text{m}_{P-T(\text{EG})}$, where EG stands for supercritical epitaxial growth. As shown in Figure S7, under reaction condition of 6 MPa and 40°C, a 400 nm-thick ZIF-8 layer with blurred crystal morphology was formed on ZnO buffer layer, while further increasing reaction temperature to 60°C led to the formation of well-intergrown ZIF-8 membrane with grain size of ~300 nm (Figure 3d) and thickness of ~500 nm (Figure 3e, 3f and Figure S8), respectively. Further increasing reaction pressure and temperature to 8 MPa and 80°C caused a further increase of grain size and thickness to 1.5 μm and 1.2 μm , respectively (Figure 3g and h). XRD patterns (Figure 3i) indicated that all obtained membranes belonged to pure ZIF-8 phase.

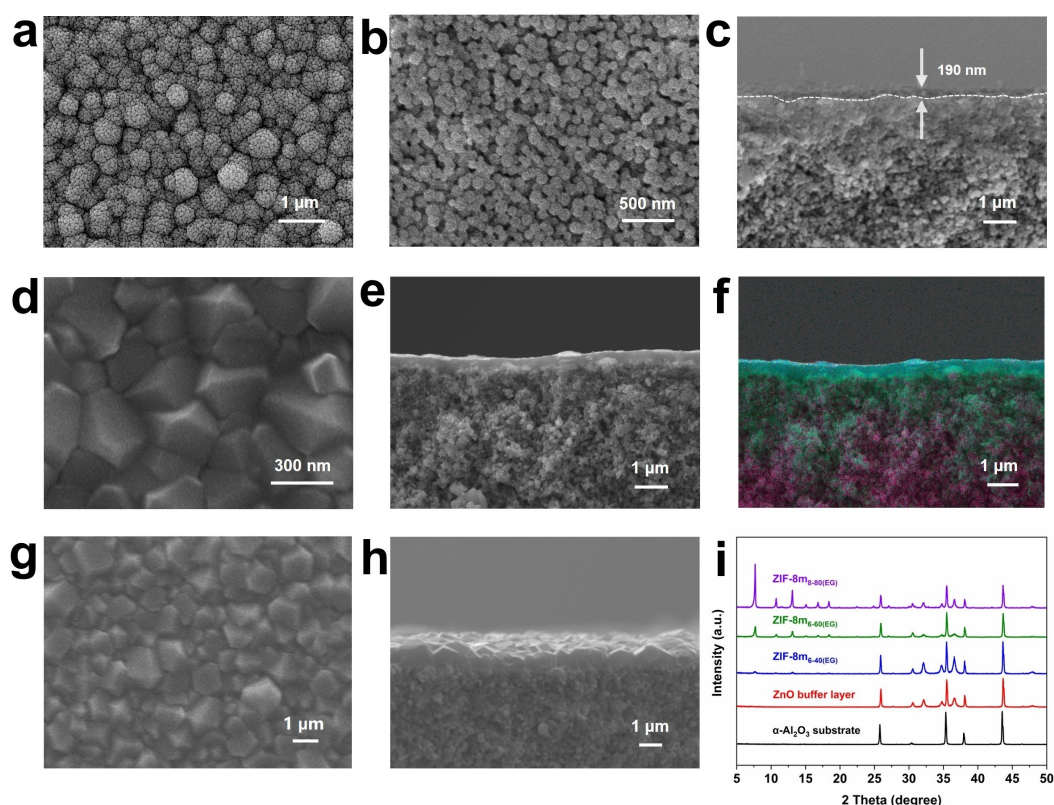


Figure 3. (a) SEM image of ZnO buffer layer. (b, c) SEM images of ZIF-8 seed layer. (d, e) SEM images and (f) EDXS mapping (Al = red, Zn = green) of ZIF-8 $m_{6-60(EG)}$. (g, h) SEM images of ZIF-8 $m_{8-80(EG)}$. (i) XRD patterns of porous α - Al_2O_3 substrate, ZnO buffer layer and ZIF-8 membranes obtained under varying conditions.

To further distinguish the structural discrepancy between scC_2H_6 -synthesized ZIF-8 membrane and $scCO_2$ -synthesized ZIF-8 membrane, both samples were thinned using Focused Ion Beam (FIB). Relevant HAADF-STEM images further

confirmed that the obtained membrane was not only well-intergrown but also well embedded in substrate pores (Figure 4a and S9). HR-TEM characterization of specific regions was then conducted. To be more specific, ZIF-8

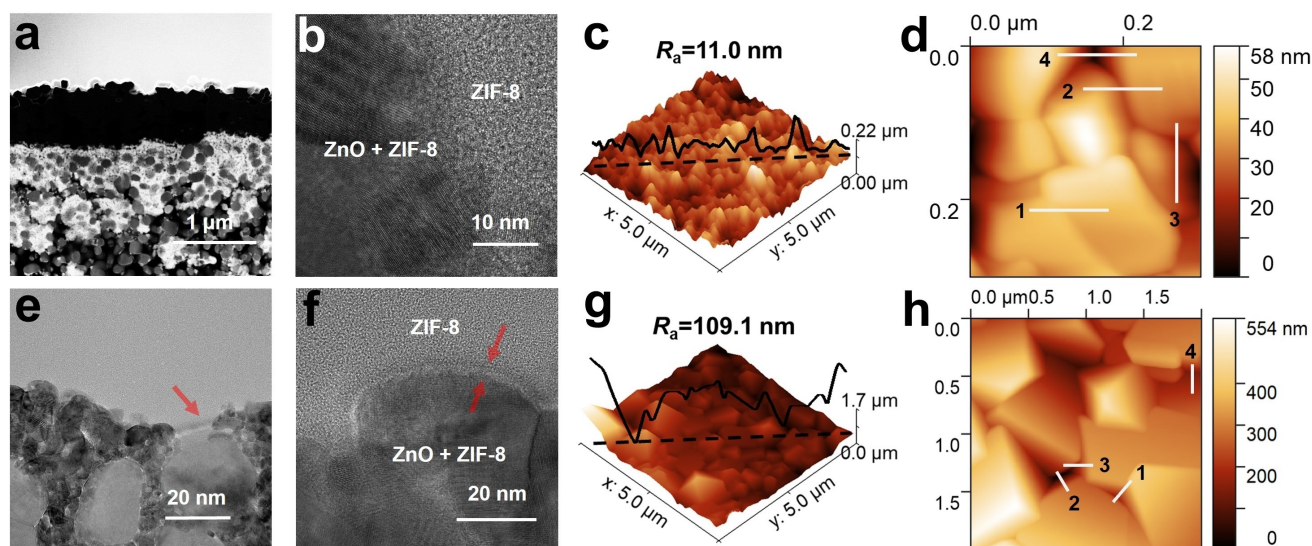


Figure 4. (a) HAADF-STEM image, (b) cross-sectional HR-TEM image and (c, d) AFM spectra of scC_2H_6 -synthesized ZIF-8 $m_{6-60(EG)}$ membrane. (e, f) Cross-sectional HR-TEM images and (g, h) AFM spectra of $scCO_2$ -synthesized ZIF-8 $m_{10-95(EG)}$ membrane.

membrane prepared via scC_2H_6 processing showed no obvious grain boundary defects between ZIF-8 crystallites and ZnO nanocrystals (Figure 4b), implying that non-selective diffusion pathway in the membrane had been eliminated. This may be attributed to the neutrality of the reaction medium (i.e., scC_2H_6), which was non-corrosive to the interfacial structure.^[18b,c] Furthermore, AFM characterization was conducted for qualitative evaluation of the size of intercrystalline defects in the membrane. As shown in Figure 4c and d, ZIF-8 membrane prepared through scC_2H_6 processing showed R_a value of 11.0 nm with sharp profile. In contrast, conspicuous grain boundary defects (denoted with red arrows) existed between ZIF-8 crystallites and ZnO nanocrystals in scCO_2 -synthesized ZIF-8 membrane (Figure 4e and f). This could be attributed to the corrosive acidic environment caused by partial dissolution of scCO_2 in H_2O generated during ZIF-8 forming (i.e., $\text{ZnO} + 2\text{mIm} \rightarrow \text{ZIF-8} + \text{H}_2\text{O}$). Simultaneously, corresponding AFM spectra revealed that its R_a value reached 109.1 nm (Figure 4g) with relatively obscure profile (Figure 4h). In terms of the degree of intergrowth between adjacent ZIF-8 crystallites, we found that surface height fluctuation in scC_2H_6 -synthesized ZIF-8 membrane (≤ 50 nm, Figure S10a) was much lower than that of scCO_2 -synthesized counterpart (≤ 150 nm, Figure S10b). Obviously, low roughness and sharp profile of scC_2H_6 -synthesized ZIF-8 membrane compared with scCO_2 -synthesized counterpart were beneficial for eliminating non-selective grain boundary defects.

Based on the intensity of diffraction peaks of ZIF-8 phase at 7.4° (denoted as I_m) and wurtzite ZnO phase at 31.9° (denoted as I_b), the C_R of deposited ZnO buffer layer could be evaluated in terms of the ratio of I_m to I_b (I_m/I_b). Our calculation results indicated that the value of I_m/I_b gradually increased with increasing temperature and pressure (Figure 5a), e.g., from 0.3 (ZIF-8 $\text{m}_{6-60(\text{EG})}$) to 7.1 (ZIF-8 $\text{m}_{8-80(\text{EG})}$). Although complete ZnO conversion could not be achieved due to the shielding effect of dense top ZIF-8 layer, its presence in substrate pores, which represented a clear reflection of defect-free nature of newly formed ZIF-8 layer, was beneficial for the formation of semi-confined structure of obtained ZIF-8 membrane with enhanced mechanical strength.

Our previous studies revealed that the change in membrane morphology was closely related to physicochemical properties of SCFs. As shown in Figure S11 and S12, the

viscosity of C_2H_6 steeply decreased from 0.041 cp (30°C) to 0.015 cp (60°C) under pressure of 6 MPa. Further increasing the temperature led to a plateau of viscosity curve, implying a negligible influence of reaction temperature on its viscosity. The viscosity and density of scC_2H_6 under the reaction condition of 6 MPa and 60°C were the lowest compared with other reaction conditions, which was more conducive to homogeneous dispersion of ligands in the reaction zone. In addition, we noted that its physicochemical properties had obvious advantages compared with scCO_2 . According to our previous research, the optimal scCO_2 reaction condition was 10 MPa and 95°C , which was used as the standard of reference. We found that under scC_2H_6 condition of 6 MPa and 60°C , its density reached $111.9 \text{ kg}\cdot\text{m}^{-3}$, which was $\sim 50\%$ lower than that of scCO_2 ($195.4 \text{ kg}\cdot\text{m}^{-3}$) accompanying with 31.4 % reduction in viscosity (Figure 5b). Even so, ligand solubility in scC_2H_6 remained higher than that in scCO_2 (65 and $41 \text{ mg}\cdot\text{L}^{-1}$, respectively), demonstrating higher affinity of scC_2H_6 solvent for organic ligands compared with scCO_2 . Therefore, maintaining scC_2H_6 at 6 MPa and 60°C should be more favorable for the preparation of defect-free ZIF-8 membranes, relying on higher nutrient concentration, higher solvent diffusivity, and lower ligand diffusion resistance; moreover, as shown in Table S2, the growth rate of ZIF-8 membrane in scC_2H_6 reaction medium at 6 MPa and 60°C was calculated to be $0.02 \mu\text{m}/\text{h}$, which was lower than common solvents due to lower ligand deprotonation rate. Owing to their difference in ZnO dissolution rate, the growth rate of ZIF-8 membranes in scC_2H_6 was lower than that in scCO_2 with no compromise in viscosity-dependent ligand diffusion rate, enabling more precise control over ZIF-8 nucleation and growth kinetics in scC_2H_6 reaction medium, which was beneficial for reducing grain boundary defects in the membrane.

The $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ separation performance of obtained ZIF-8 membrane was subsequently evaluated with a Wicke-Kallenbach permeation cell (Figure S13). Under initial reaction conditions of 6 MPa and 40°C , higher scC_2H_6 viscosity (0.028 cp) and lower 2-mIm solubility ($25 \text{ mg}\cdot\text{L}^{-1}$) resulted in only $\sim 9.8\%$ ZnO conversion (Figure 5a and b), while residual ZnO nanoparticles embedded in the ZIF-8 layer not only severely reduced C_3H_6 -accessible micropores as evidenced by lower BET surface areas of ZnO@ZIF-8 powders (Figure 2i), but also led to insufficient Zn^{2+} nutrient supply and poor intergrowth, giving rise to relatively low $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ separation factor ($\text{SF}=19.8$) and C_3H_6 permeance ($\sim 2.0 \times 10^{-9} \text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$) of ZIF-8 $\text{m}_{6-40(\text{EG})}$ (Figure 6a). Further increasing reaction temperature to 60°C resulted in increased solubility ($65 \text{ mg}\cdot\text{L}^{-1}$) and decreased viscosity (0.015 cp) of scC_2H_6 (Figure 5b), thereby contributing to increased diffusivity of 2-mIm. As a result, the ZnO C_R was increased to 37.8 % accompanying with reduced grain boundary defects. Correspondingly, the $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8$ selectivity and C_3H_6 permeance of ZIF-8 $\text{m}_{6-60(\text{EG})}$ increased to 150 and $5.8 \times 10^{-9} \text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$, respectively. In contrast, increasing reaction pressure and temperature to 8 MPa and 80°C resulted in higher ZnO C_R of 69.2 % at the expense of uncontrollable ZIF-8 nucleation

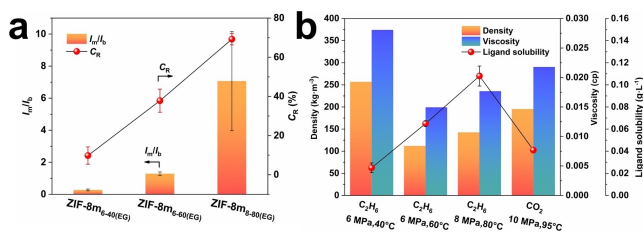


Figure 5. (a) I_m/I_b and C_R of ZIF-8 membranes synthesized under varying conditions (the values are averaged over ten samples). (b) Comparison of the density, viscosity and solubility of scCO_2 and scC_2H_6 under varying conditions (the values are averaged over three samples).

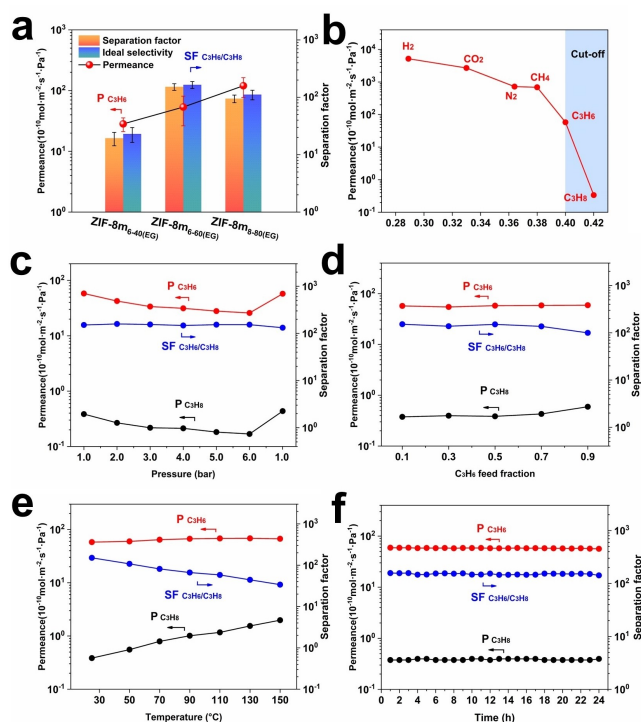


Figure 6. (a) The C₃H₆/C₃H₈ separation performance of ZIF-8 membranes obtained under varying conditions. Gas permeation results of ZIF-8 m_{6-60(EG)} in terms of (b) single gas permeance, (c) operation pressure, (d) C₃H₆ feed fraction, (e) operation temperature, and (f) long-term stability.

and growth kinetics, which was detrimental to grain boundary defect elimination. As a result, the C₃H₆ permeance of ZIF-8 m_{8-80(EG)} increased to $1.1 \times 10^{-8} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ at the expense of lower C₃H₆/C₃H₈ selectivity of 104.6. Therefore, maintaining appropriate 2-mIm solubility and scC₂H₆ viscosity towards appropriate ZnO C_R was indispensable for synthesizing ZIF-8 membranes with optimized membrane structure and superior C₃H₆/C₃H₈ separation performance.

We further investigated gas permeation properties of ZIF-8 m_{6-60(EG)} in more details. Single gas permeation results indicated that permeances of all gas molecules steadily decreased with increasing kinetic diameters (Figure 6b). The ideal selectivity of H₂/N₂, H₂/CO₂, H₂/CH₄ and H₂/C₃H₆ gas pairs reached 7.2, 2.0, 7.5 and 89.5 with H₂ permeance of $5.2 \times 10^{-7} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$. Of particular note, its ideal C₃H₆/C₃H₈ selectivity reached 172.1 with C₃H₆ permeance of $5.9 \times 10^{-9} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$, implying a sharp “cut-off” effect and therefore, defect-free nature of obtained membrane.

The influence of operation pressure and C₃H₆ feed fraction on the C₃H₆/C₃H₈ separation performance of ZIF-8 m_{6-60(EG)} was further investigated, where the flux of C₃H₆ (mol·m⁻²·s⁻¹) was used to characterize the gain effect of high pressure on gas flow rate. Gas permeation results implied that ZIF-8 m_{6-60(EG)} maintained stable selectivity (153.2) upon increasing operation pressure to 6 bar (Figure 6c) while the C₃H₆ flux increased from 5.8×10^{-4} to $1.6 \times 10^{-3} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$, which was advantageous for operation

at higher pressure (Table S4 and S5). Simultaneously, the effect of feed pressure on the C₃H₆/C₃H₈ separation performance of scCO₂-synthesized ZIF-8 membrane (at 10 MPa and 95 °C) was investigated for comparison. Gas permeation results indicated that obtained ZIF-8 membrane showed significant reduction in C₃H₆/C₃H₈ selectivity upon increasing the feed pressure to 4 bar (Figure S14) while keeping C₃H₆ permeance largely unchanged. Further increasing pressure to 6 bar, however, led to a significant increase of C₃H₆ permeance (from $2.2 \times 10^{-8} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{bar}^{-1}$ at 1 bar to $4.3 \times 10^{-8} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{bar}^{-1}$ at 6 bar) at the expense of unceasing decline in C₃H₆/C₃H₈ selectivity (from 51.8 at 1 bar to 2.1 at 6 bar). This could possibly be attributed to weak acidic environment caused by dissolution of CO₂ in H₂O generated during membrane processing, resulting in generation of intergranular gaps in the membrane and therefore, inferior C₃H₆/C₃H₈ separation performance.^[21]

To the best of our knowledge, this represented the first report on the preparation of pressure-resistance ZIF-8 membranes via SCF processing. Regarding the influence of feed composition, gas permeation results showed that its C₃H₆/C₃H₈ selectivity was quite stable under varying feed composition. For instance, upon increasing C₃H₆ feed fraction from 10 % to 90 %, the C₃H₆/C₃H₈ selectivity only slightly reduced from 151.1 to 100 (Figure 6d), which remained fully met the criteria for 80 % reduction in energy consumption in comparison with cryogenic distillation.^[22] Regarding the effect of operation temperature ranging between 25 and 150 °C, our results showed that with increasing temperature, C₃H₈ showed higher degree of increase in permeance than C₃H₆ (115.6 % and 51.5 %, respectively), resulting in reduced C₃H₆/C₃H₈ selectivity (Figure 6e). Finally, operation stability of ZIF-8 m_{6-60(EG)} was investigated. Our results showed that both C₃H₆ permeance ($5.8 \times 10^{-9} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$) and C₃H₆/C₃H₈ separation factor (151.1) remained stable within 24 h (Figure 6f), which was indicative of excellent operation stability.

Conclusions

In this study, scC₂H₆ was used as reaction medium of ZIF-8 membranes during epitaxial SCF processing. Owing to high mass transfer performance and chemical inertness of reaction medium, grain boundary defects were largely omitted, resulting in the formation of ZIF-8 membranes with superior and pressure-resistance C₃H₆/C₃H₈ separation performance. The ZIF-8 membrane synthesized under optimum conditions achieved an ideal C₃H₆/C₃H₈ selectivity as high as 172.1; of particular note, the C₃H₆/C₃H₈ selectivity can be well maintained even at operation pressure up to 6 bar under varying feed composition. Our research reveals that varying the type of SCFs represented an effective for microstructure optimization and performance enhancement of MOF membranes.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords: Supercritical ethane · ZIF-8 membrane · Paraffin/olefin separation · Microstructure

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