Epitaxial supercritical fluid processing of ZIF-8 membranes towards efficient C\textsubscript{3}H\textsubscript{6}/C\textsubscript{3}H\textsubscript{8} separation

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A B S T R A C T

Although having shown promising prospects in diverse gas separations, sustainable fabrication of high-performance metal-organic framework (MOF) membranes remains a significant challenge towards applications. In the present work, epitaxial supercritical fluid (SCF) processing was developed for preparing highly C\textsubscript{3}H\textsubscript{6}-permeative ZIF-8 membranes by direct deposition of ZIF-8 seed layers followed by epitaxial supercritical growth in supercritical CO\textsubscript{2} (scCO\textsubscript{2}) environments. Our results indicated that maintaining scCO\textsubscript{2} in the gas-like region was indispensable for preparing ZIF-8 membranes with desired microstructure and superior C\textsubscript{3}H\textsubscript{6}/C\textsubscript{3}H\textsubscript{8} separation (i.e., C\textsubscript{3}H\textsubscript{6} permeance and C\textsubscript{3}H\textsubscript{8}/C\textsubscript{3}H\textsubscript{6} selectivity). Simultaneously, unreacted 2-methylimidazole ligands could be fully recycled and reutilized after epitaxial SCF processing. The present study sheds light on the future prospects for sustainable production of versatile high-performance MOF membranes.

1. Introduction

Light olefin/paraffin separation represents one of the most energy consuming processes in the petroleum industry [1–5]. In comparison with conventional cryogenic distillation, membrane-based separation has been considered as a promising alternative due to its energy efficiency, environment friendliness, easy operation, and small footprint [6–9]. Among them, polycrystalline ZIF-8 membranes exhibited the attractive prospects in C\textsubscript{3}H\textsubscript{6}/C\textsubscript{3}H\textsubscript{8} separation due to well-defined pore aperture, structural flexibility, abundant functionality, and excellent stability [10]. To date, a variety of solution-based synthetic methods have been proposed for the fabrication of ZIF-8 membranes with attractive C\textsubscript{3}H\textsubscript{6}/C\textsubscript{3}H\textsubscript{8} separation performances [11–24]. Nonetheless, improper disposal of waste mother liquor and unreacted reagents made it less attractive for batch production and commercial application. Therefore, developing new synthetic methods enabling sustainable production of high-quality ZIF-8 membranes has become indispensable.

As an alternative to traditional protocols, supercritical fluid (SCF) processing has shown tremendous potential for sustainable production of high-quality MOF membranes considering unique physicochemical properties of SCFs like controllable phase transition, high diffusivities, tunable solubility, and chemical inertness [25–30]. Through in situ SCF processing, we prepared C\textsubscript{3}H\textsubscript{6}-permeative ZIF-8 membranes by direct treatment of ZnO buffer layer-modified porous α-Al\textsubscript{2}O\textsubscript{3} substrates with 2-methylimidazole (2-mlm) ligands in supercritical CO\textsubscript{2} (scCO\textsubscript{2}) environments [28]. One unique advantage of SCF processing was that both used SCF solvents and residual 2-mlm ligands could be facilely and fully recovered, facilitating the realization of zero pollutant discharge. Nevertheless, we believe that there still remains vast space of improvement on their C\textsubscript{3}H\textsubscript{6}/C\textsubscript{3}H\textsubscript{8} separation performances; accordingly, further innovation in ZIF-8 membrane processing is urgently required.

Compared with in situ SCF processing, epitaxial SCF processing of ZIF-8 membranes, which involves the deposition of ZIF-8 seed layers followed by their epitaxial growth in SCF environments, is expected to exert more precise control over their microstructure due to the effective decoupling of nucleation and growth procedures [31–34], resulting in not only significant reduction in membrane thickness but also better intergrowth between neighboring ZIF-8 crystallites, which is quite beneficial for improving their C\textsubscript{3}H\textsubscript{6}/C\textsubscript{3}H\textsubscript{8} separation performances. In
the present work, we aimed to prepare highly C₃H₆-permselective ZIF-8 membranes with well-controlled microstructure via epitaxial SCF processing (Fig. 1). ScCO₂ is chosen as the reaction medium because of the intrinsic chemical inertness, environmental friendliness, reaction condition mildness, low cost, and easy availability [35,36]. As will be described below, our results indicated that employing epitaxial SCF processing led to the formation of ZIF-8 membranes with significantly enhanced C₃H₆/C₃H₈ separation performances; moreover, maintaining scCO₂ in the gas-like region during epitaxial SCF processing was found indispensable for preparing ZIF-8 membranes with desired microstructure.

The aforementioned ZIF-8 membrane was fabricated as follows (Fig. 1): Initially, a ZnO buffer layer, which served as the exclusive metal source of the ZIF-8 membrane, was directly deposited on the surface of porous α-Al₂O₃ substrate. Subsequently, slip-coating method was employed for depositing uniform ZIF-8 seed layer on the above modified substrate. In the next step, the seeded substrate was placed in a home-made reaction cell containing powdered 2-mIm ligands where epitaxial supercritical growth was carried out. After completion of the reaction, both unreacted 2-mIm ligands and gaseous CO₂ were recycled, and prepared ZIF-8 membrane was directly characterized and tested without any post-treatment procedures (e.g., washing, drying and activation).

2. Experimental section

2.1. Deposition of ZnO buffer layers

Sol-gel method was employed for the deposition of ZnO buffer layers on porous α-Al₂O₃ substrates [37]. Initially, Zn-based solution was obtained by addition of 2100.0 mg zinc acetate to 12.0 ml 2-methoxyethanol, followed by stirring at 70 °C for 30 min. Afterwards, 0.6 ml monoethanolamine was slowly dropped to the above Zn-based solution, followed by stirring at room-temperature (RT) for 10 h. In the next step, the pre-cleaned asymmetric porous α-Al₂O₃ substrates were subjected to spin-coating (3000 rpm, 1 min) with obtained Zn-based sol, followed by drying at 70 °C for 10 min. Finally, the above surface-modified porous α-Al₂O₃ disks were calcined at 400 °C for 2 h before use.

2.2. Deposition of ZIF-8 seed layers

ZIF-8 nanoparticles (~70 nm) were prepared as reported in previous literature [38]. Initially, 734.4 mg zinc nitrate hexahydrate and 810.6 mg 2-mIm were dispersed in 50.0 ml methanol, respectively. Then the above-prepared solutions were mixed quickly with stirring, and mainly kept at RT for 24 h. After completion of the reaction, the obtained white precipitates were collected via repeated centrifugation, washing with methanol, and drying overnight.

Slip-coating was employed for depositing ZIF-8 seed layers on ZnO buffer layer-modified porous α-Al₂O₃ substrates [11]. Initially, ZIF-8 seed suspension (0.2 wt%) was obtained by dispersing wet ZIF-8 nanoparticles into methanol, followed by sonication for 30 min. Subsequently, ZnO-modified substrates were immersed in the seed solution for 20 s, and then carefully extracted. Finally, seeded substrates were dried at 70 °C for 6 h before use.

2.3. Preparation of ZIF-8 membranes via epitaxial SCF processing

Initially, 400.0 mg downsizing (ground for 10 min) 2-mIm powders were spread out uniformly at the bottom of a home-made semi-permeable cylindrical cell (Fig. S1) [28]. Subsequently, seeded substrates were placed horizontally above the aforementioned reaction cell with the surface modified-seed layer side facing down. In the next step, several sealed reaction cells were placed inside the SCF apparatus (SFT-110 XW). Finally, gaseous CO₂ was poured into SCF vessel, and then spontaneous transformed to scCO₂ fluid under given reaction conditions (details were shown in SI-3). Epitaxial SCF growth was maintained for 24 h. After completion of the reaction, residual powders left in the chamber were recycled and freshly obtained ZIF-8 membranes were directly used for characterization and tests [39] without any post-treatment procedures.

3. Results and discussion

3.1. Preparation of ZIF-8 membranes

The first step was the deposition of ZnO buffer layers, which not only smoothened the porous α-Al₂O₃ substrate surface (Fig. 2a) but also served as the exclusive zinc source of ZIF-8 membranes. Among various methods, sol-gel technique was employed due to its efficiency,
simplicity, low cost, and easy scale-up [37]. As shown in Fig. 2b and c, a compact ZnO layer with grain size of ~30 nm was successfully obtained. The EDXS patterns implied that obtained ZnO layer partially infiltrated into underlying porous α-Al₂O₃ substrate, which was advantageous for maintaining a high adhesion strength (Fig. S2 and S3). Relevant XRD pattern demonstrated that the obtained buffer layer indeed belonged to pure ZnO phase (Fig. S4) [40]. The corresponding gas permeation results confirmed that surface modification with the ZnO buffer layer exerted a negligible influence on gas permeation behavior of the substrate (Table S1).

Subsequently, 70 nm-sized ZIF-8 nanocrystals, which were prepared by following a previous literature (Fig. S5 and S6) [38], were uniformly deposited on the above ZnO modified substrate by slip-coating method [11]. SEM results indicated that a uniform, 95 nm-thick ZIF-8 seed layer was obtained (Fig. 2d–f).

In the next step, epitaxial SCF growth was conducted at 95 °C and 100 bar to seal intergranular gaps in the seed layer. As shown in Fig. 2g and i and Fig. S7, a well-intergrown ZIF-8 membrane could be obtained under optimal scCO₂ processing conditions. Cross-sectional SEM results confirmed that average thickness of prepared membrane was 390 nm, which was thinner than the previous in situ SCF-processed ZIF-8 membrane [28]. In addition, relevant XRD pattern indicated that a pure ZIF-8 membrane had been obtained (Fig. S4) [41]. Corresponding ATR-IR spectrum (Fig. S8) implied that no detectable 2-mIm powders were attached to the freshly prepared ZIF-8 membrane since accompanying with the gasification of scCO₂ after epitaxial SCF processing, 2-mIm powders were simultaneously removed from the pores or surface of the ZIF-8 membrane. Thus, any post-treatment procedures (e.g., washing, drying and activation) normally applied in conventional ZIF-8 membrane synthetic methods were no longer necessary, which was quite advantageous for their bath production and commercial application.

3.2. Sustainability of epitaxial SCF processing

In addition to ZIF-8 membranes, precipitates recovered (recovery rate: 96.4%) at the bottom of the reaction cells after epitaxial SCF processing were characterized. As shown in Fig. S9, the morphology of residual white powders was in good accordance with pristine 2-mIm ligands. Relevant XRD patterns also confirmed that pure 2-mIm powders had been collected (Fig. 3a); moreover, ATR-IR and XPS results indicated that there was no evidence of the existence of Zn species (like ZnO or ZIF-8 phase) within recovered powders (Fig. 3b and c). To verify their reusability, recovered 2-mIm ligands were again employed in epitaxial SCF processing. As illustrated in Fig. 3d and Fig. S10, continuous ZIF-8 membrane with no discernible gain boundary defects was successfully obtained, thus indicating the effectiveness of epitaxial SCF processing in preparing ZIF-8 membrane in a sustainable manner.
3.3. Gas separation performance of ZIF-8 membranes

Finally, gas permeation properties of the aforementioned ZIF-8 membrane prepared in optimal gas-like scCO$_2$ environments (95 °C and 100 bar) were investigated using a Wicke-Kallenbach setup. It was observed that the H$_2$ permeance of prepared ZIF-8 membrane attained $8.8 \times 10^{-7}$ mol m$^{-2}$ s$^{-1}$ Pa$^{-1}$, which was higher than that of other larger-sized gas molecules [42], and its ideal H$_2$/N$_2$, H$_2$/CH$_4$, H$_2$/C$_3$H$_8$ and H$_2$/C$_3$H$_6$ selectivity reached 10.9, 11.5, 54.8 and 4288 (Fig. 4a), respectively. Taking into consideration of the significance of

Fig. 3. (a) XRD patterns and (b) ATR-IR spectra of (i) raw and (ii) recovered 2-mIm ligands. (c) XPS spectrum of recovered 2-mIm ligands. (d) SEM image of ZIF-8 membrane prepared by epitaxial SCF processing in GLS region (at 95 °C and 100 bar) with recovered 2-mIm powders.

Fig. 4. (a) Single gas permeance of ZIF-8 membrane prepared by epitaxial SCF processing in GLS region (at 95 °C and 100 bar). The inset shows ideal selectivity and separation factor of ZIF-8 membrane. (b) Comparison of C$_3$H$_6$/C$_3$H$_8$ separation performance of ZIF-8 membrane prepared in GLS region (at 95 °C and 100 bar) with previous literatures (Table S3). (c-e) The binary C$_3$H$_6$/C$_3$H$_8$ separation performances of ZIF-8 membrane prepared in GLS region (at 95 °C and 100 bar) as a function of (c) operating temperature (v/v = 1/1), (d) C$_3$H$_6$ feed fraction (v/v from 1/9 to 9/1), (e) operation pressure (v/v = 1/1). (f) Long-term operation stability of ZIF-8 membrane for C$_3$H$_6$/C$_3$H$_8$ (v/v = 1/1) separation under ambient conditions.
energy-efficient C₅H₆/C₇H₈ separation in petrochemical industry, C₃H₆/C₇H₈ permeation properties of the obtained ZIF-8 membrane were further investigated. The ideal C₅H₆/C₇H₈ selectivity of the ZIF-8 membrane reached 78.2 with a remarkable C₃H₆ permeance of 1.6 × 10⁻⁸ mol m⁻² s⁻¹ Pa⁻¹, which was not only superior to previous in situ SCF-processed ZIF-8 membrane [28], but also comparable with most porous α-Al₂O₃-supported ZIF-8 membranes synthesized with other synthetic methods (Fig. 4b, details were shown in Table S3), thus confirming the great significance of epitaxial SCF processing in enhancing the C₅H₆/C₇H₈ permeability of ZIF-8 membranes, owing to the introduction of closely packed ZIF-8 seed layer.

In addition, the effect of operation temperature, C₃H₆ feed fraction, and operation pressure on C₅H₆/C₇H₈ permeation properties of the obtained ZIF-8 membrane was studied in detail (Fig. 4c-e). It was observed that both C₃H₆ permeance and C₅H₆/C₇H₈ SF were negatively associated with operation temperature (Fig. 4c), owing to the difference in apparent activation energy for the permeation of C₃H₆ and C₇H₈ through the membrane [11, 14]. For instance, increasing operation temperature from RT to 150 °C led to considerable decrease in both C₃H₆ permeance (from 1.5 × 10⁻⁸ to 1.0 × 10⁻⁸ mol m⁻² s⁻¹ Pa⁻¹) and C₅H₆/C₇H₈ SF (from 51.8 to 24.4). While the C₃H₆ permeance and C₅H₆/C₇H₈ SF strongly depended on the C₃H₆ feed fraction (Fig. 4d), owing to the effect of pressure on adsorption isotherm and/or decreased diffusion selectivity in the ZIF-8 framework with increasing loading [11, 14]. For instance, increasing the C₃H₆ concentration from 10% to 90% led to considerable decrease in both C₃H₆ permeance (from 1.6 × 10⁻⁸ to 1.5 × 10⁻⁸ mol m⁻² s⁻¹ Pa⁻¹) and C₅H₆/C₇H₈ SF (from 56.6 to 30.1). In addition, SF of equimolar C₅H₆/C₇H₈ gas pair was found to inevitably fluctuate with operation pressure (Fig. 4e), owing to the pressure-induced gate-opening phenomenon and/or the existence of grain boundary defects in ZIF-8 membranes [14]. For example, SF of the C₅H₆/C₇H₈ gas pair dropped sharply from 51.8 to 6.7 with elevating pressure (from 1.0 to 2.0 bar), while the C₃H₆ permeance (~1.5 × 10⁻⁸ mol m⁻² s⁻¹ Pa⁻¹) remained unchanged. Finally, long-term operation results showed that both C₃H₆ permeance (~1.5 × 10⁻⁸ mol m⁻² s⁻¹ Pa⁻¹) and C₅H₆/C₇H₈ SF (~51) remained unchanged within 24 h (Fig. 4f), thus confirming a remarkable durability of our ZIF-8 membrane.

3.4. Elucidation of the structure-performance relationship

It should be emphasized that precisely controlling epitaxial SCF processing conditions (i.e., reaction temperature and pressure) was of vital importance to tailor the C₅H₆/C₇H₈ separation performance of produced ZIF-8 membranes (Fig. 5, Figs. S11 and S12). Of particular note, maintaining the scCO₂ reaction medium in gas-like scCO₂ (GLS, below the Widom line [43], Fig. 5a) region, which was featured with physicochemical properties approximate to gaseous CO₂ (i.e., lower density and viscosity, Fig. 5b–d), was found indispensable for preparing highly C₃H₆-permselective ZIF-8 membranes (Fig. 5e and f). A further in-depth investigation of the influence of reaction conditions on their C₅H₆/C₇H₈ separation performances implied that well-integrated ZIF-8 membranes with considerable C₅H₆/C₇H₈ selectivity (>35) could be obtained as long as the reaction conditions fell in the GLS region (Fig. 5f, Figs. S11 and S12); in contrast, carrying out reaction in liquid-like scCO₂ (LLS, above the Widom line [43], Fig. 5a) region, which possessed physicochemical properties similar to liquid CO₂ (e.g., higher density and viscosity, Fig. 5b–d), led to the fabrication of poorly-permselective ZIF-8 membranes displaying inferior C₅H₆/C₇H₈ selectivity (<10, Fig. 5e and f, Figs. S11 and S12).

Obviously, the large discrepancy in the C₅H₆/C₇H₈ permselectivity of prepared ZIF-8 membranes could be attributed to different physicochemical properties of the scCO₂ reaction medium in GLS and LLS regions, which significantly modulated the microstructure of ZIF-8 membranes (Fig. 2g–i, 6a-d, and Fig. S11). To be more specific, it is well recognized that both density and viscosity of scCO₂ increase with increasing pressure at constant temperature (Fig. 5c and d). On the one hand, increasing pressure from 100 to 500 bar lead to increased density of scCO₂ in LLS region (Fig. 5b), giving rise to enhanced solubility of 2-mIm ligands (details were shown in SI-16 [44], Fig. 5d) from 0.041 (GLS region) to 1.543 g/L (LLS region) at 95 °C and therefore, more sufficient supply of nutrients; correspondingly, the thickness of ZIF-8 membranes increased remarkably from 0.4 (GLS region) to 4.4 µm (LLS region) at 95 °C (Figs. 2i and 6b), while the C₃H₆ permeance reduced sharply from 1.5 × 10⁻⁸ (GLS region) to 1.4 × 10⁻⁹ mol m⁻² s⁻¹ Pa⁻¹ (LLS region) as shown in Fig. 5e. On the other hand, higher pressure led to increased viscosity of scCO₂ in LLS region (Fig. 5c), resulting in lower diffusivity of 2-mIm ligands in intergranular gaps of ZIF-8 membranes and therefore,

Fig. 5. (a) Phase diagram of CO₂ highlighting the supercritical fluid region (blue-red line: Widom line of scCO₂, calculation details were shown in SI-17), and synthetic conditions in NCS, LLS, and GLS regions. (b–f) The structure-performance relationship between (b–d) physicochemical properties of scCO₂ and (e, f) C₅H₆/C₇H₈ separation performances of ZIF-8 membranes prepared by epitaxial SCF processing under different scCO₂ conditions.
more efficient preservation of intercrystalline defects (shown in Fig. 6a); accordingly, the \( \text{C}_3\text{H}_6/\text{C}_3\text{H}_8 \) selectivity was remarkably decreased from 51.8 (GLS region) to 4.1 (LLS region) at 95°C (Fig. 5f). Similar conclusions could be drawn from ZIF-8 membranes prepared under other scCO\(_2\) conditions either (e.g., at 65°C with pressure ranging from 100 to 500 bar, Fig. 5 and Fig. S11).

Simultaneously, it seems to be very difficult to produce highly \( \text{C}_3\text{H}_6/\text{C}_3\text{H}_8 \) selective ZIF-8 membranes in near-critical scCO\(_2\) (NCS) region (Fig. 5a), which showed anomalous physicochemical properties. For instance, a poorly-intergrown ZIF-8 membrane with inferior \( \text{C}_3\text{H}_6/\text{C}_3\text{H}_8 \) selectivity of only 2.4 was obtained at the temperature and pressure of 32°C and 75 bar (NCS region, Figs. 5f and 6c and d). This was understandable, since although the solubility (0.029 g/L) and viscosity (0.026 cp) of scCO\(_2\) in NCS region were similar to those in GLS region (e.g., solubility of 0.041 g/L and viscosity of 0.022 cp for scCO\(_2\) at 95°C and 100 bar, Fig. 5c and d), lower reaction temperature in NCS region resulted in insufficient supply of nutrients and therefore, the fabrication of defective ZIF-8 membrane with inferior \( \text{C}_3\text{H}_6/\text{C}_3\text{H}_8 \) selectivity.

In addition to scCO\(_2\), we further tried epitaxially growing ZIF-8 membranes in gaseous or liquid CO\(_2\) environments. Nevertheless, it turned out to be impossible to completely seal the open space in seed layers (Figs. S13–16). Therefore, conducting epitaxial supercritical growth in GLS region, where 2-mIm ligands exhibited lower solubility but higher diffusivity in scCO\(_2\) environments, was more favorable for preparing ZIF-8 membranes with advantageous microstructure and superior \( \text{C}_3\text{H}_6/\text{C}_3\text{H}_8 \) separation performances.

4. Conclusions

To summarize, epitaxial SCF processing was developed in this study for sustainable fabrication of highly \( \text{C}_3\text{H}_6 \)-perselective ZIF-8 membranes through deposition of uniform ZIF-8 seed layers followed by epitaxial growth in scCO\(_2\) environments. Of particular note, maintaining scCO\(_2\) in GLS region warranted the production of continuous ZIF-8 membranes displaying enhanced ideal \( \text{C}_3\text{H}_6/\text{C}_3\text{H}_8 \) selectivity (78.2) and \( \text{C}_3\text{H}_8 \) permeance \((1.6 \times 10^{-8} \text{ mol m}^{-2} \text{s}^{-1} \text{ Pa}^{-1})\). Furthermore, both unreacted 2-mIm ligands and discharged CO\(_2\) could be easily recycled and reutilized in high-quality ZIF-8 membrane production, therefore, zero pollutant discharge was achieved. We believe that epitaxial SCF processing could serve as a powerful tool for sustainable fabrication of versatile high-performance MOF membranes.

Credit author statement

Liangliang Liu: Finished major experiments and relevant characterizations. Taotao Ji: Assisted in drawing the schematic illustration and the morphological characterization. Wenjing Hu: Helped with the epitaxial supercritical fluid processing. Yanwei Sun and Yongfu He: Helped with the analysis of experimental data. Jiahui Yan: Helped with the gas permeation test. Gaohong He: Assisted in analyzing the experimental data. Yi Liu: Conceived the idea, projected relevant experiments, and jointly wrote the manuscript with contributions from all authors.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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