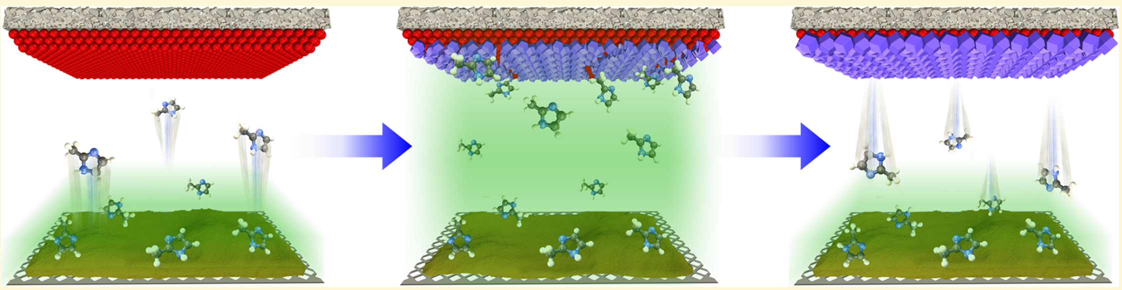
ACS MATERIALS LETTERS

www.acsmaterialsletters.org

Beyond Solution-Based Protocols: MOF Membrane Synthesis in Supercritical Environments for an Elegant Sustainability Performance Balance

Liangliang Liu, Yifan Song, Taotao Ji, Yanwei Sun, Demin He, Haoquan Hu, and Yi Liu*

Cite This: *ACS Materials Lett.* 2020, 2, 1142−1147



ABSTRACT: **Supercritical fluids (SCFs) represent materials at temperatures and pressures above their critical points where distinct liquid and gas phases do not exist. SCFs possess several unique properties rendering them excellently adapted for the reaction medium of MOF membranes (like ZIF-8) which, although offering an energy-efficient and eco-friendly option for large-scale industrial separation, are still experiencing a dilemma between process sustainability and performance superiority. In this study we addressed this issue through a facile SCF synthetic protocol employing supercritical CO_2 ($scCO_2$) as the reaction medium. Relying on the near-zero surface tension, low viscosity, and high diffusivity of $scCO_2$, nanoscale intercrystalline defects could be effectively patched, resulting in the formation of well-intergrown ZIF-8 membranes with commercially attractive olefin/paraffin (C_3H_6/C_3H_8) separation performance. Moreover, after the SCF processing, both discharged CO_2 and unreacted ligands could be conveniently recovered and reutilized, resulting in zero pollutant discharge due to the controllable phase transition, variable solubility, and chemical inertness of $scCO_2$. This work sheds lights on the promising prospects of SCF processing for sustainable fabrication of high-performing MOF membranes.**

Synthetic membranes have been widely utilized in diverse industrially relevant separation processes because of their obvious superiority over traditional thermal-driven distillation process in terms of energy efficiency, operation simplicity, environment friendliness, and small footprint.[1−6] Polymer membranes, although being widespread employed in diverse industrial separation applications, commonly suffered from intrinsic permeability selectivity trade-off, fouling, degradation, or material failure upon operating under harsh conditions.[7] In this regard, metal−organic framework (MOF) membranes not only complement existing polymer membranes but also open new possibilities for industrial separation applications, relying on the well-defined pore aperture, tailorable pore size, versatile functionality, structural robustness, and high thermal/chemical stability.[8−15] Taking ZIF-8 membranes,[16] one of the most extensively studied MOF membranes as an example, a variety of solution[17−22] and vapor[23] based synthetic protocols have been developed for the preparation of ZIF-8 membranes with commercially attractive C_3H_6/C_3H_8 selectivity (>35). Nevertheless, it remained a great challenge for balancing process sustainability and performance superiority. For instance, diverse solution-based synthetic methods (such as aqueous solution processing,[17] contra-diffusion synthesis,[18] sol−gel synthesis,[19] current-driven syn-

Received: June 19, 2020
Accepted: August 12, 2020
Published: August 12, 2020

https://dx.doi.org/10.1021/acsmaterialslett.0c00267
ACS Materials Lett. 2020, 2, 1142−1147

thesis,[20] and interfacial microfluidic processing[21]) easily enabled the formation of well-intergrown ZIF-8 membranes exhibiting exceptional C_3H_6/C_3H_8 selectivity. In a recent research, Nair et al.[22] prepared several types of all-nanoporous hybrid membranes (ANHMs) through combing ZIF-8 with MFI nanoparticles/nanosheets. Compared with single-phase ZIF-8 membranes, prepared ANHMs exhibited concurrently increased C_3H_6 permeability and C_3H_6/C_3H_8 selectivity; moreover, high-performance ANHMs were fabricated with simple methods on low-cost supports, which was potentially advantageous for their large-scale production. However, improper disposal and discharge of spent mother liquor not only caused serious environmental pollution but also made it impractical to recover solvents and unreacted reagents from the spent mother liquor. The above problems must be overcome before delving into practical applications. It should be noted that Jeong et al.[19a] reported vapor-phase defect-induced ripening of ZIF-8 seed layers in the presence of ligand vapor. Obtained ZIF-8 membranes not only became well-intergrown but also exhibited unprecedented C_3H_6/C_3H_8 selectivity (~120). This method held great promise for facile synthesis of high-performance ZIF-8 membranes in an economical and sustainable manner. Recently Tsapatsis et al.[23b] pioneered the preparation of highly C_3H_6/C_3H_8 selective ZIF-8 membranes through an all-vapor-phase processing method, which was conceptually very attractive.

The above-mentioned dilemma inspired us to develop new synthetic protocols to better balance process sustainability and performance superiority.[24] Supercritical fluids (SCFs), which represent materials at temperatures and pressures above their critical points where distinct liquid and gas phases do not exist, possess properties between those of liquids and gases. As an alternative to conventional solvents, SCFs have been widely used in a range of industrial and laboratory processes.[25] It is noticed, however, that to date, SCFs have not been utilized as platform for MOF membrane synthesis,[26] although they hold great promise for the sustainable production[27] because of the following unique properties: (1) near-zero surface tension, low viscosity, and high diffusivity, which facilitate fast diffusion of reagents in nanoscale intercrystalline defects and easy defect patching through further crystal growth in SCF environments, and (2) controllable phase transition and variable solubility. Since simply altering the operating temperature and pressure in the vicinity of critical points enables facile transition of fluids between supercritical and gaseous states, after the completion of membrane preparation in SCF environments, phase segregation between gaseous fluids and solid solute occurs spontaneously upon evacuation of the reaction chamber so that both SCFs and unreacted reagents can be easily recovered and reutilized, thereby making it possible to realize zero pollutant discharge.

As a demonstration of this concept, in this study we aim to prepare ZIF-8 membranes displaying attractive C_3H_6/C_3H_8 separation performance via novel SCF processing (Figure 1a). Supercritical carbon dioxide ($scCO_2$) is chosen as the reaction medium due to the reaction condition mildness (P_c = 73.8 bar, T_c = 31.1 °C) and intrinsic chemical inertness. Moreover, CO_2 as a major greenhouse gas is easily available from carbon capture and storage (CCS) plants, which is expected to break the trade-off between environmental protection and economic viability.[28] As will be discussed below, our experiments indicated that employing $scCO_2$ as the reaction medium led to the formation of well-intergrown ZIF-8 membranes with commercially attractive C_3H_6/C_3H_8 separation performance.

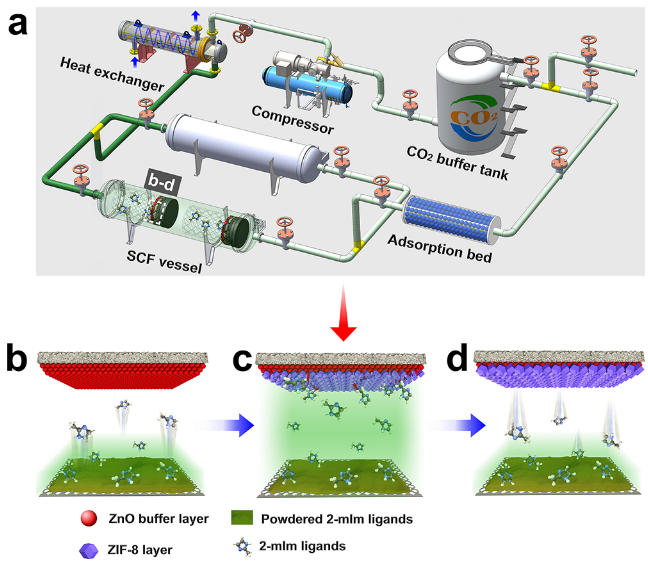


Figure 1. (a) Schematic illustration of proposed SCF processing of ZIF-8 membrane with zero pollutant discharge on a macroscopic scale. (b−d) Schematic illustration of in situ supercritical growth of ZIF-8 membrane with sustainable nutrient recovery on a mesoscopic scale.

The whole fabrication process was briefly described as follows (Figure 1b−d, experimental details are elaborated in the Supporting Information): Initially, a uniform ZnO buffer layer was predeposited on porous α-Al_2O_3 substrate, which not only significantly promoted the heterogenous nucleation density of ZIF-8 crystallites but also served as exclusive metal source of ZIF-8 membrane. Subsequently, ZnO buffer layer-modified porous α-Al_2O_3 substrate was horizontally placed in a deliberately designed semi-permeable cylindrical cell containing given amount of 2-methylimidazole (2-mIm). In the next step, gaseous CO_2 was discharged in stainless-steel reaction chamber and spontaneously transformed to $scCO_2$ in which "supercritical growth" was carried out (Figure 1b and 1c). Finally, after the completion of supercritical growth, both gaseous CO_2 discharged from the chamber and unreacted 2-mIm ligands left in the chamber could be conveniently recovered (Figure 1a and 1d).

Initially, a ZnO buffer layer was deposited on porous α-Al_2O_3 substrate prior to supercritical growth. Among various ZnO buffer layer deposition methods, the sol−gel method was employed in this study due to its simplicity, adaptability, and ecofriendliness.[29] SEM images indicated that prepared ZnO buffer layer was continuous and highly uniform (Figures 2a and S1). The XRD pattern showed three conspicuous diffraction peaks at 31.9°, 34.7°, and 36.4°, which could be assigned to the reflections of hexagonal wurtzite ZnO phase (Figure 3b).[30]

Subsequently, in situ supercritical growth was conducted to convert ZnO buffer layer into ZIF-8 membrane. Initially, the reaction was carried out directly in the SCF vessel. Nevertheless, it turned out to be very difficult to prepare well-intergrown ZIF-8 membrane since the stainless-steel reaction chamber volume was too large, resulting in a low concentration of 2-mIm (Figures S2 and S3). To increase 2-mIm concentration at the ZnO buffer layer-$scCO_2$ interface, we deliberately designed a semi-permeable cylindrical cell in which

https://dx.doi.org/10.1021/acsmaterialslett.0c00267
ACS Materials Lett. 2020, 2, 1142−1147

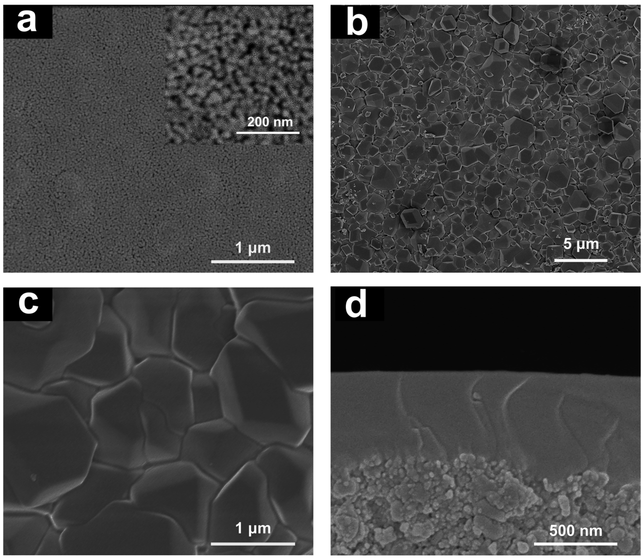


Figure 2. SEM images of (a) ZnO buffer layer and (b–d) ZIF-8 membrane obtained by in situ supercritical growth in $scCO_2$ environments.

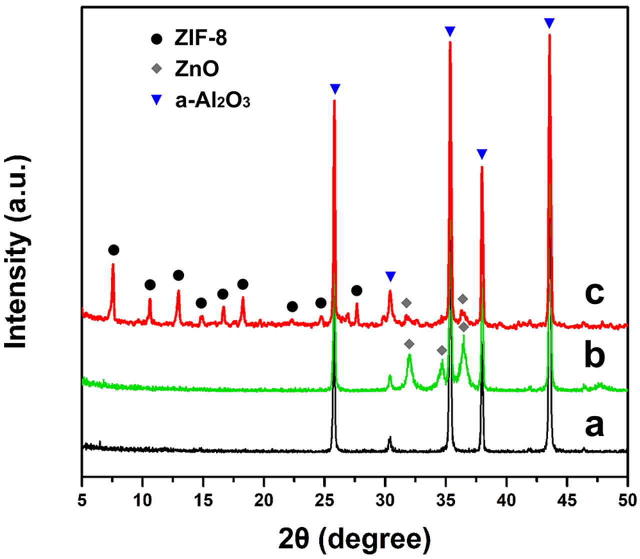


Figure 3. XRD patterns of (a) porous α-Al_2O_3 substrate, (b) ZnO buffer layer, and (c) ZIF-8 membrane obtained by in situ supercritical growth in $scCO_2$ environments.

the ZnO buffer layer-modified substrate was placed (Figure S4). Two factors were found crucial for warranting the formation of well-intergrown ZIF-8 membrane: (1) Suitable pore size of the semi-permeable cylindrical cell. In principle, the pore size should be large enough for guaranteeing the free diffusion of $scCO_2$ molecules while small enough for confining powdered 2-mIm ligands in the cylindrical cell. (2) The relative position between substrate and powdered 2-mIm ligands. During SCF processing, the substrate should be horizontally placed on top of the cylindrical cell with the ZnO buffer layer-modified side facing down, while powdered 2-mIm ligands should be placed at the bottom of the cylindrical cell. Owing to the near-zero surface tension, low viscosity, and high diffusivity of $scCO_2$, under supercritical conditions 2-mIm was enabled to diffuse rapidly across nanoscale intercrystalline defects in ZIF-8 membrane and permitted to eliminate these defects via regulated coordination with Zn^{2+} ions released from remaining unreacted ZnO buffer layer underneath, which was necessary to enhance the C_3H_6/C_3H_8 separation performance of prepared ZIF-8 membrane.

After in situ supercritical growth under the optimal reaction condition, a well-intergrown 600 nm-thick ZIF-8 membrane with an average grain size of 850 nm was formed (Figure 2b–d). The corresponding XRD pattern illustrated that obtained membrane indeed belonged to pure ZIF-8 phase (Figure 3c). Moreover, it was noted that diffraction peaks derived from the ZnO phase still existed even after the completion of supercritical growth. The incomplete conversion of ZnO buffer layer could be ascribed to the rapid formation of defect-free protective ZIF-8 top layer during SCF processing, which effectively prevented further nucleophilic attack of 2-mIm molecules on remaining ZnO buffer layer underneath as convinced by our previous study.[30] In addition, we noted that no residual powders (i.e., 2-mIm ligands) were adhered on the surface of fresh ZIF-8 membrane since accompanying with evacuation of the reaction chamber and gasification of $scCO_2$, 2-mIm ligands occluded inside the pores or adsorbed on the surface of ZIF-8 membrane were simultaneously removed. Therefore, any post-treatment steps (e.g., activation and washing) commonly involved in solution-based synthetic protocols were no longer necessary, which was quite beneficial to industrial scale production.

In addition to ZIF-8 membrane, white powders collected at the bottom of the reaction chamber after completion of the reaction was studied further. The absence of any impure diffraction peaks in the 2θ range of 5–50° convincingly demonstrated that recovered powders belonged to pure 2-mIm phase (Figure S5). Afterwards, recovered 2-mIm powders were again used in the preparation of ZIF-8 membrane to assess their reusability. The experimental results indicated that prepared ZIF-8 membrane remained continuous and well-intergrown with no discernible intercrystalline defects (Figure S6 and S7), thereby demonstrating the competence of SCF processing in sustainable and green ZIF-8 membrane production.

Finally, gas permeation properties of freshly prepared ZIF-8 membrane were studied using a Wicke–Kallenbach setup[30,31] (Figure S8) and related results were summarized in Figure 4. Single gas permeation test indicated that gas permeability through the ZIF-8 membrane clearly depended on kinetic diameters of gas molecules (Figure 4a); moreover, the ideal selectivity of H_2/N_2, H_2/CH_4, H_2/C_3H_6, and H_2/C_3H_8 gas pairs reached 13.2, 13.6, 83.0, and 1456.5, respectively, which were all far above their Knudsen selectivity (Figures 4a, S9, and S10), thereby clearly indicating the dominance of size-based molecular sieving mechanism.[32] It should be noted that although the limiting aperture size of ZIF-8 was estimated to be 0.34 nm, gas molecules with larger kinetic diameters including N_2 (0.364 nm), CH_4 (0.38 nm), C_3H_6 (0.40 nm), and C_3H_8 (0.42 nm) could still permeate through the membrane due to intrinsic breathing and gate-opening phenomena of ZIF-8 framework.[32,33] Considering the significance of energy-efficient C_3H_6/C_3H_8 separation in petroleum refinery industry, the C_3H_6/C_3H_8 separation performance of prepared ZIF-8 membrane was studied further. Gas permeation results indicated that separation factor (SF) of equimolar C_3H_6/C_3H_8 gas mixture through ZIF-8 membrane reached 47.1 with a C_3H_6 permeance of 29.2×10^{-10} mol·m^{-2}·s^{-1}·Pa^{-1} (Figure 4b), which not only notably outperformed the

https://dx.doi.org/10.1021/acsmaterialslett.0c00267
ACS Materials Lett. 2020, 2, 1142–1147

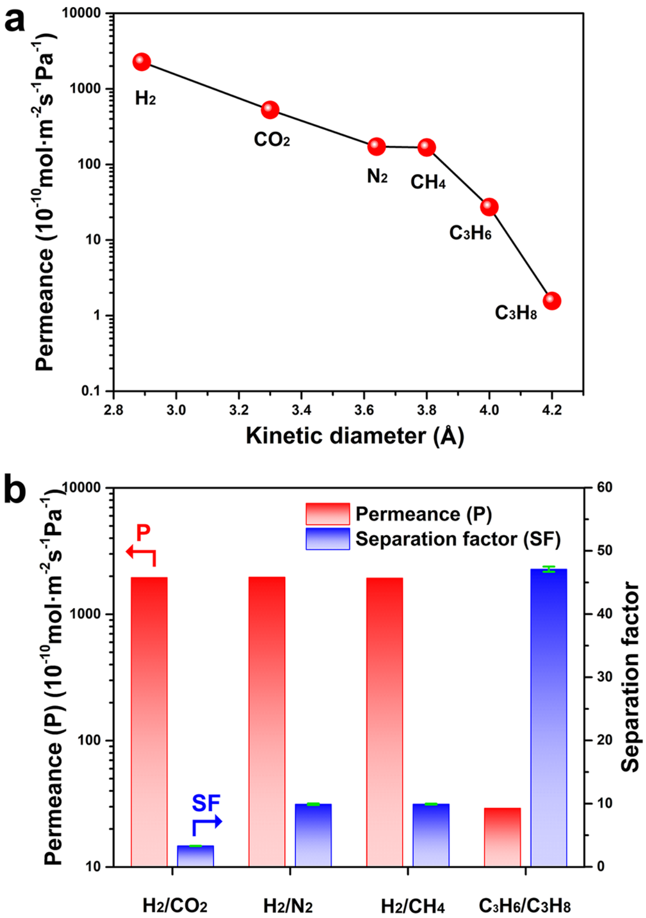


Figure 4. (a) Permeances of single gases through ZIF-8 membrane under ambient conditions as a function of molecular kinetic diameters of gas molecules. (b) Permeances and separation factor of different equimolar gas mixtures through ZIF-8 membrane under ambient conditions.

upper bound limits for polymeric membranes,[34] but also easily met the proposed performance criteria for commercial applications (Figure S11).[18a] It was noticed that the C_3H_6 permeance was lower than that of some reported ZIF-8 membranes prepared with liquid synthetic protocols, probably owing to the incomplete conversion of ZnO buffer layers, the existence of amorphous ZIF deposit, and the formation of possible blocked regions caused by residual 2-mIm ligands as evidenced by previous research.[17b,18c,23b,30] Meanwhile, effects of permeation temperature, feed composition, and total feed pressure on the C_3H_6/C_3H_8 separation performance of prepared ZIF-8 membrane were investigated and main conclusions were as follow: (1) Both the permeance of C_3H_6 and SF of equimolar C_3H_6/C_3H_8 gas mixture decreased with the increase of operating temperature (Figure S12). (2) The permeance of C_3H_6 and SF of binary C_3H_6/C_3H_8 gas mixture slightly decreased with the increase of the molar fraction of C_3H_6 in the feed gas (Figure S13). 3) The permeance of C_3H_6 steadily increased, while SF of equimolar C_3H_6/C_3H_8 gas mixture decreased with the increase of total feed pressure (Figure S14). Finally, long-term operation stability of ZIF-8 membrane was studied. Our results indicated that both gas permeances and SF of equimolar gas mixture were constant within 24 h under ambient conditions (Figures S15 and S16). All the above results convincingly demonstrated that ZIF-8 membranes prepared via SCF processing held great promise for industrial C_3H_6/C_3H_8 separation.

To sum up, in this study SCF processing was first employed in sustainable production of ZIF-8 membrane with attractive C_3H_6/C_3H_8 separation performance via in situ supercritical growth. Near-zero surface tension, low viscosity, and high diffusivity of $scCO_2$ enabled effective intercrystalline defect patching; while controllable phase transition, variable solubility, and chemically inertness of $scCO_2$, as well as mildness of reaction conditions warranted facile recovery and reutilization of both discharged CO_2 and unreacted 2-mIm ligands resulting in zero pollutant discharge. More importantly, our research implied that $scCO_2$, an ideal reaction medium of ZIF-8 membranes, was easily available from CCS plants so that the trade-off between environmental protection and economic viability could be satisfactorily solved. We believe that SCF processing holds great potential to serve as a powerful tool for sustainable preparation of various MOF membranes with superior separation performances in the future.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmaterialslett.0c00267.

Experimental procedures, characterization data, and gas separation performance of ZIF-8 membranes (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Yi Liu − *State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China;* orcid.org/0000-0002-2073-4832; Email: diligenliu@dlut.edu.cn

Authors

Liangliang Liu − *State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China*

Yifan Song − *State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China*

Taotao Ji − *State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China*

Yanwei Sun − *State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China*

Demin He − *State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China*

Haoquan Hu − *State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China;* orcid.org/0000-0002-5288-2186

Complete contact information is available at: https://pubs.acs.org/10.1021/acsmaterialslett.0c00267

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors are grateful to National Natural Science Foundation of China (21176231), Liaoning Revitalization

Talents Program (XLYC1807084), Fok Ying-Tong Education Foundation of China (171063), and the Technology Innovation Team of Dalian University of Technology (DUT2017TB01) for the financial support.

■ REFERENCES

(1) Koros, W. J.; Zhang, C. Materials for Next-Generation Molecularly Selective Synthetic Membranes. *Nat. Mater.* **2017**, *16*, 289−297.

(2) (a) Carta, M.; Malpass-Evans, R.; Croad, M.; Rogan, Y.; Jansen, J. C.; Bernardo, P.; Bazzarelli, F.; McKeown, N. B. An Efficient Polymer Molecular Sieve for Membrane Gas Separations. *Science* **2013**, *339*, 303−307. (b) Kim, H. W.; Yoon, H. W.; Yoon, S. M.; Yoo, B. M.; Ahn, B. K.; Cho, Y. H.; Shin, H. J.; Yang, H.; Paik, U.; Kwon, S.; Choi, J. Y.; Park, H. B. Selective Gas Transport through Few-Layered Graphene and Graphene Oxide Membranes. *Science* **2013**, *342*, 91−95. (c) Bachman, J. E.; Smith, Z. P.; Li, T.; Xu, T.; Long, J. R. Enhanced Ethylene Separation and Plasticization Resistance in Polymer Membranes Incorporating Metal-Organic Framework Nanocrystals. *Nat. Mater.* **2016**, *15*, 845−849. (d) Denning, S.; Lucero, J.; Koh, C. A.; Carreon, M. A. Chabazite Zeolite SAPO-34 Membranes for He/CH_4 Separation. *ACS Mater. Lett.* **2019**, *1*, 655−659.

(3) Peng, Y.; Li, Y.; Ban, Y.; Jin, H.; Jiao, W.; Liu, X.; Yang, W. Metal- Organic Framework Nanosheets as Building Blocks for Molecular Sieving Membranes. *Science* **2014**, *346*, 1356−1359.

(4) Varoon, K.; Zhang, X.; Elyassi, B.; Brewer, D. D.; Gettel, M.; Kumar, S.; Lee, J. A.; Maheshwari, S.; Mittal, A.; Sung, C. Y.; Cococcioni, M.; Francis, L. F.; McCormick, A. V.; Mkhoyan, K. A.; Tsapatsis, M. Dispersible Exfoliated Zeolite Nanosheets and Their Application as a Selective Membrane. *Science* **2011**, *334*, 72−75.

(5) Jeon, M. Y.; Kim, D.; Kumar, P.; Lee, P. S.; Rangnekar, N.; Bai, P.; Shete, M.; Elyassi, B.; Lee, H. S.; Narasimharao, K.; Basahel, S. N.; Al-Thabaiti, S.; Xu, W.; Cho, H. J.; Fetisov, E. O.; Thyagarajan, R.; Dejaco, R. F.; Fan, W.; Mkhoyan, K. A.; Siepmann, J. I.; Tsapatsis, M. Ultra-Selective High-Flux Membranes from Directly Synthesized Zeolite Nanosheets. *Nature* **2017**, *543*, 690−694.

(6) Shinde, D. B.; Sheng, G.; Li, X.; Ostwal, M.; Emwas, A. H.; Huang, K. W.; Lai, Z. Crystalline 2D Covalent Organic Framework Membranes for High-Flux Organic Solvent Nanofiltration. *J. Am. Chem. Soc.* **2018**, *140*, 14342−14349.

(7) Park, H. B.; Kamcev, J.; Robeson, L. M.; Elimelech, M.; Freeman, B. D. Maximizing the Right Stuff: The Trade-off between Membrane Permeability and Selectivity. *Science* **2017**, *356*, eaab0530.

(8) Liu, Y.; Ng, Z.; Khan, E. A.; Jeong, H.-K.; Ching, C.-b.; Lai, Z. Synthesis of Continuous MOF-5 Membranes on Porous α-Alumina Substrates. *Microporous Mesoporous Mater.* **2009**, *118*, 296−301.

(9) Sun, Y.; Liu, Y.; Caro, J.; Guo, X.; Song, C.; Liu, Y. In-Plane Epitaxial Growth of Highly c-Oriented NH_2-MIL-125(Ti) Membranes with Superior H_2/CO_2 Selectivity. *Angew. Chem., Int. Ed.* **2018**, *57*, 16088−16093.

(10) Sun, Y.; Song, C.; Guo, X.; Liu, Y. Concurrent Manipulation of Out-of-Plane and Regional In-Plane Orientations of NH_2-UiO-66 Membranes with Significantly Reduced Anisotropic Grain Boundary and Superior H_2/CO_2 Separation Performance. *ACS Appl. Mater. Interfaces* **2020**, *12*, 4494−4500.

(11) Liu, Y.; Pan, J. H.; Wang, N.; Steinbach, F.; Liu, X.; Caro, J. Remarkably Enhanced Gas Separation by Partial Self-Conversion of a Laminated Membrane to Metal-Organic Frameworks. *Angew. Chem.* **2015**, *127*, 3071−3075.

(12) Rangnekar, N.; Mittal, N.; Elyassi, B.; Caro, J.; Tsapatsis, M. Zeolite Membranes - a Review and Comparison with MOFs. *Chem. Soc. Rev.* **2015**, *44*, 7128−7154.

(13) Qiu, S.; Xue, M.; Zhu, G. Metal-Organic Framework Membranes: From Synthesis to Separation Application. *Chem. Soc. Rev.* **2014**, *43* (16), 6116−6140.

(14) Lin, Y. Metal Organic Framework Membranes for Separation Applications. *Curr. Opin. Chem. Eng.* **2015**, *8*, 21−28.

(15) Liu, Y.; Ban, Y.; Yang, W. Microstructural Engineering and Architectural Design of Metal−Organic Framework Membranes. *Adv. Mater.* **2017**, *29*, 1606949.

(16) (a) Park, K. S.; Ni, Z.; Cote, A. P.; Choi, J. Y.; Huang, R.; Uribe-Romo, F. J.; Chae, H. K.; O'Keeffe, M.; Yaghi, O. M. Exceptional chemical and thermal stability of zeolitic imidazolate frameworks. *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103*, 10186−10191. (b) Bux, H.; Liang, F.; Li, Y.; Cravillon, J.; Wiebcke, M.; Caro, J. Zeolitic Imidazolate Framework Membrane with Molecular Sieving Properties by Microwave-Assisted Solvothermal Synthesis. *J. Am. Chem. Soc.* **2009**, *131*, 16000−16001. (c) Yao, J.; Wang, H. Zeolitic Imidazolate Framework Composite Membranes and Thin Films: Synthesis and Applications. *Chem. Soc. Rev.* **2014**, *43*, 4470−4493.

(17) (a) Pan, Y.; Li, T.; Lestari, G.; Lai, Z. Effective Separation of Propylene/Propane Binary Mixtures by ZIF-8 Membranes. *J. Membr. Sci.* **2012**, *390*−*391*, 93−98. (b) Wei, R.; Chi, H. Y.; Li, X.; Lu, D.; Wan, Y.; Yang, C. W.; Lai, Z. Aqueously Cathodic Deposition of ZIF-8 Membranes for Superior Propylene/Propane Separation. *Adv. Funct. Mater.* **2020**, *30*, 2070042.

(18) (a) Kwon, H. T.; Jeong, H. K. In Situ Synthesis of Thin Zeolitic-Imidazolate Framework ZIF-8 Membranes Exhibiting Exceptionally High Propylene/Propane Separation. *J. Am. Chem. Soc.* **2013**, *135*, 10763−10768. (b) Kwon, H. T.; Jeong, H. K.; Lee, A. S.; An, H. S.; Lee, J. S. Heteroepitaxially Grown Zeolitic Imidazolate Framework Membranes with Unprecedented Propylene/Propane Separation Performances. *J. Am. Chem. Soc.* **2015**, *137*, 12304−12311. (c) Lee, M. J.; Kwon, H. T.; Jeong, H. K. High-Flux Zeolitic Imidazolate Framework Membranes for Propylene/Propane Separation by Postsynthetic Linker Exchange. *Angew. Chem., Int. Ed.* **2018**, *57*, 156−161.

(19) (a) Kwon, H. T.; Jeong, H. K.; Lee, A. S.; An, H. S.; Lee, T.; Jang, E.; Lee, J. S.; Choi, J. Defect-Induced Ripening of Zeolitic-Imidazolate Framework ZIF-8 and Its Implication to Vapor-Phase Membrane Synthesis. *Chem. Commun.* **2016**, *52*, 11669−11672. (b) Li, W.; Wu, W.; Li, Z.; Shi, J.; Xia, Y. Sol-Gel Asynchronous Crystallization of Ultra-Selective Metal-Organic Framework Membranes for Gas Separation. *J. Mater. Chem. A* **2018**, *6*, 16333−16340. (c) Yu, J.; Pan, Y.; Wang, C.; Lai, Z. ZIF-8 Membranes with Improved Reproducibility Fabricated from Sputter-Coated ZnO/Alumina Supports. *Chem. Eng. Sci.* **2016**, *141*, 119−124.

(20) Zhou, S.; Wei, Y.; Li, L.; Duan, Y.; Hou, Q.; Zhang, L.; Ding, L. X.; Xue, J.; Wang, H.; Caro, J. Paralyzed Membrane: Current-Driven Synthesis of a Metal-Organic Framework with Sharpened Propene/Propane Separation. *Sci. Adv.* **2018**, *4*, eaau1393.

(21) Brown, A. J.; Brunelli, N. A.; Eum, K.; Rashidi, F.; Johnson, J. R.; Koros, W. J.; Jones, C. W.; Nair, S. Interfacial Microfluidic Processing of Metal-Organic Framework Hollow Fiber Membranes. *Science* **2014**, *345*, 72−75.

(22) (a) Rashidi, F.; Leisen, J.; Kim, S. J.; Rownaghi, A. A.; Jones, C. W.; Nair, S. All-Nanoporous Hybrid Membranes: Redefining Upper Limits on Molecular Separation Properties. *Angew. Chem., Int. Ed.* **2019**, *58*, 236−239. (b) Eum, K.; Yang, S.; Min, B.; Ma, C.; Drese, J. H.; Tamhankar, Y.; Nair, S. All-Nanoporous Hybrid Membranes: Incorporating Zeolite Nanoparticles and Nanosheets with Zeolitic Imidazolate Framework Matrices. *ACS Appl. Mater. Interfaces* **2020**, *12*, 27368−27377.

(23) (a) Li, W.; Su, P.; Li, Z.; Xu, Z.; Wang, F.; Ou, H.; Zhang, J.; Zhang, G.; Zeng, E. Ultrathin Metal-Organic Framework Membrane Production by Gel-Vapour Deposition. *Nat. Commun.* **2017**, *8*, 406. (b) Ma, X.; Kumar, P.; Mittal, N.; Khlyustova, A.; Daoutidis, P.; Mkhoyan, K. A.; Tsapatsis, M. Zeolitic Imidazolate Framework Membranes Made by Ligand-Induced Permselectivation. *Science* **2018**, *361*, 1008−1011.

(24) Zimmerman, J. B.; Anastas, P. T.; Erythropel, H. C.; Leitner, W. Designing for a Green Chemistry Future. *Science* **2020**, *367*, 397−400.

(25) Eckert, C. A.; Knutson, B. L.; Debenedetti, P. G. Supercritical Fluids as Solvents for Chemical and Materials Processing. *Nature* **1996**, *383*, 313−318.

(26) (a) Matsuyama, H.; Yano, H.; Maki, T.; Teramoto, M.; Mishima, K.; Matsuyama, K. Formation of Porous Flat Membrane by Phase Separation with Supercritical CO_2. *J. Membr. Sci.* **2001**, *194*, 157−163. (b) Liu, Y. F.; Xu, Q. Q.; Wang, Y. Q.; Zhu, H. Y.; Yin, J. Z. Preparation of Supported Ionic Liquid Membranes Using a Supercritical Fluid Deposition Method and Study of the Capillary Phase Transition of Ionic Liquids in Supercritical CO_2. *Ind. Eng. Chem. Res.* **2019**, *58*, 19189−19196.

(27) (a) Nelson, A. P.; Farha, O. K.; Mulfort, K. L.; Hupp, J. T. Supercritical Processing as a Route to High Internal Surface Areas and Permanent Microporosity in Metal-organic Framework Materials. *J. Am. Chem. Soc.* **2009**, *131*, 458−460. (b) López-Periago, A.; Vallcorba, O.; Frontera, C.; Domingo, C.; Ayllón, J. A. Exploring a Novel Preparation Method of 1D Metal Organic Frameworks Based on Supercritical CO_2. *Dalt. Trans.* **2015**, *44*, 7548−7553. (c) Sinnwell, M. A.; Miller, Q. R. S.; Liu, L.; Tao, J.; Bowden, M. E.; Kovarik, L.; Barpaga, D.; Han, Y.; Kishan Motkuri, R.; Sushko, M. L.; Schaef, H. T.; Thallapally, P. K. Kinetics and Mechanisms of ZnO to ZIF-8 Transformations in Supercritical CO_2 Revealed by In Situ X-Ray Diffraction. *ChemSusChem* **2020**, *13*, 2602−2612.

(28) Hepburn, C.; Adlen, E.; Beddington, J.; Carter, E. A.; Fuss, S.; Mac Dowell, N.; Minx, J. C.; Smith, P.; Williams, C. K. The Technological and Economic Prospects for CO_2 Utilization and Removal. *Nature* **2019**, *575*, 87−97.

(29) Zhang, X.; Liu, Y.; Li, S.; Kong, L.; Liu, H.; Li, Y.; Han, W.; Yeung, K. L.; Zhu, W.; Yang, W.; Qiu, J. New Membrane Architecture with High Performance: ZIF-8 Membrane Supported on Vertically Aligned ZnO Nanorods for Gas Permeation and Separation. *Chem. Mater.* **2014**, *26*, 1975−1981.

(30) Liu, Y.; Peng, Y.; Wang, N.; Li, Y.; Pan, J. H.; Yang, W.; Caro, J. Significantly Enhanced Separation Using ZIF-8 Membranes by Partial Conversion of Calcined Layered Double Hydroxide Precursors. *ChemSusChem* **2015**, *8*, 3582−3586.

(31) Liu, Y.; Wang, N.; Pan, J. H.; Steinbach, F.; Caro, J. In Situ Synthesis of MOF Membranes on ZnAl-CO_3 LDH Buffer Layer-Modified Substrates. *J. Am. Chem. Soc.* **2014**, *136*, 14353−14356.

(32) Zhang, C.; Lively, R. P.; Zhang, K.; Johnson, J. R.; Karvan, O.; Koros, W. J. Unexpected Molecular Sieving Properties of Zeolitic Imidazolate Framework-8. *J. Phys. Chem. Lett.* **2012**, *3*, 2130−2134.

(33) Li, K.; Olson, D. H.; Seidel, J.; Emge, T. J.; Gong, H.; Zeng, H.; Li, J. Zeolitic Imidazolate Frameworks for Kinetic Separation of Propane and Propene. *J. Am. Chem. Soc.* **2009**, *131*, 10368−10369.

(34) Burns, R. L.; Koros, W. J. Defining the Challenges for C_3H_6/C_3H_8 Separation Using Polymeric Membranes. *J. Membr. Sci.* **2003**, *211*, 299−309.

https://dx.doi.org/10.1021/acsmaterialslett.0c00267
ACS Materials Lett. 2020, 2, 1142−1147