ACS APPLIED MATERIALS & INTERFACES

Letter

www.acsami.org

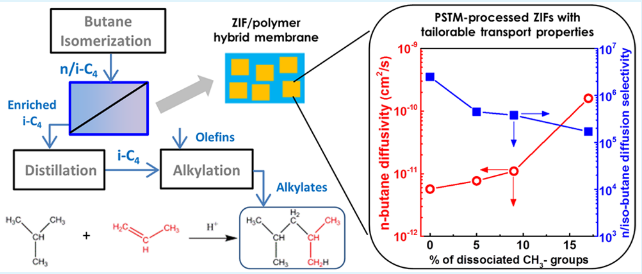
Tailoring the Transport Properties of Zeolitic Imidazolate Frameworks by Post-Synthetic Thermal Modification

Chen Zhang and William J. Koros*

School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, 311 Ferst Dr. NW, Atlanta, Georgia 30332-0100, United States

Supporting Information

ABSTRACT: Understanding how to control transport properties of zeolitic imidazolate frameworks (ZIFs) is critical to extend ZIF-based membranes and adsorbents to a wide spectrum of gas and vapor separations. In this work, we report a facile post-synthetic thermal modification (PSTM) technique to tailor ZIFs' transport properties by balancing diffusivity and diffusion selectivity. With controllable dissociation of framework methyl groups from a precursor ZIF (ZIF-8), we have prepared thermally modified ZIFs showing substantially increased *n*-butane diffusivity and attractive *n*/*iso*-butane diffusion selectivity. Hybrid ZIF/polymer mixed-matrix membranes formed using these thermally modified ZIFs are expected to deliver attractive butane isomer separation performance. Membranes based on such materials can potentially be used to retrofit refinery alkylation units for producing premium gasoline blending stocks.



KEYWORDS: *metal−organic frameworks, nanoporous materials, thermal treatment, diffusion selectivity, butane isomer separation, membrane gas separation, mixed-matrix membrane*

Zeolitic imidazolate frameworks (ZIFs) represent a family of organic−inorganic crystalline porous materials[1] comprising ZnN_4 or CoN_4 tetrahedra bridged by imidazole-based ligands. Despite topological resemblances to zeolites, ZIFs have unique molecular sieving properties. Their flexible framework[2−4] enables faster guest molecule diffusion compared with rigid zeolites possessing similar aperture size.[5,6] ZIF-8 [Zn(MeIM)$_2$, where MeIM = 2-methylimidazole] is the most extensively studied ZIF[7−9] and accounts for over 70% of the published work on ZIF-*enabled* membranes.[10] ZIF-8 has an effective aperture size of 4.0−4.2 Å and offers simultaneously attractive C_3H_6 permeability (~390 Barrer) and C_3H_6/C_3H_8 permselectivity (~130).[5] ZIF-8-based membranes with promising C_3H_6/C_3H_8 permselectivities have been successfully realized on several membrane platforms, which include supported ZIF/alumina membranes,[11−15] layered ZIF/polymer membranes,[16] and mixed-matrix ZIF/polymer membranes.[17,18] Supported ZIF-8/alumina membranes with C_3H_6/C_3H_8 mixed-gas selectivity as high as 90 have been reported.[13] Considering that C_3H_6/C_3H_8 selectivity is usually reduced in a mixture environment,[17] this is nicely consistent with ZIF-8 ideal selectivity ($\alpha[C_3H_6/C_3H_8] \sim 130$) predicted by single-component kinetic sorption measurements in large ZIF-8 crystals. The consistency further proves the validity of screening ZIF membrane materials based on independent kinetic uptake measurements of free-standing ZIF crystals.

The successful demonstration of ZIF-8 for C_3H_6/C_3H_8 separation has motivated researchers to develop ZIFs with transport properties tailored for a targeted separation.[19] It is of substantial interest to develop membrane materials for butane isomer (*n*- and *iso*-butane) separation, which is an important yet energy-intensive separation in refineries.[20] Despite ZIF-8's remarkably high *n*/*iso*-butane diffusion selectivity (2.5×10^6), *n*-butane diffusivity is only 5.7×10^{-12} cm^2/s, which makes its *n*-butane permeability commercially unattractive.[5,21] A recent study[19] reported synthesis of hybrid ZIFs by mixing linkers of ZIF-8 (MeIM) and ZIF-90 (carboxyaldehyde-2-imidazole). By variation of the linker ratio during synthesis, a controllable linker percentage and increased *n*-butane diffusivity were obtained in hybrid ZIFs.

To develop ZIFs with tailorable transport properties, an alternative to the above mixed-linker synthesis is post-synthetic modification. Gadipelli and co-workers[22] studied thermogravimetric analysis−mass spectrometry (TGA−MS) of ZIF-8 samples heated up to 800 °C. In contrast to the common belief that ZIF-8 is thermally stable up to 500 °C,[23] the TGA−MS results showed that methyl groups (on MeIM linkers) dissociate from the framework at temperatures as low as 350−400 °C. The dissociation, which was confirmed by a weakening of the $\delta(CH_3)$ mode at 1384 cm^{-1}, became increasingly rapid as the thermal treatment temperature was further increased to the 400−500 °C range. Long-range crystal order was maintained for the sample heated at 500 °C for 6 h, as evidenced by the unchanged powder X-ray diffraction (PXRD)

Received: August 20, 2015
Accepted: October 9, 2015
Published: October 9, 2015

DOI: 10.1021/acsami.5b07769
ACS Appl. Mater. Interfaces 2015, 7, 23407−23411

pattern at low 2θ angles. The thermally treated ZIF showed substantially increased CO_2 uptake and CO_2/N_2 selectivity; however, the effects of methyl group dissociation on guest molecule diffusion were not studied. Because the linker dimension controls the ZIF's effective aperture size, we believe that thermally induced methyl group dissociation and, consequently, linker size reduction can be used to "open up" the ZIF's aperture and create ZIFs with increased guest molecule diffusivity and permeability. It should be noted that similar aperture enlargement can also be realized using solvent-assisted linker exchange.[24]

Six thermally modified ZIF samples were prepared by heating the precursor ZIF (ZIF-8) at 200, 300, 400, 450, 475, and 500 °C for 2 h in a Q50 thermogravimetric analyzer (TA Instruments, New Castle, DE) under a continuous argon purge. The detailed heating protocol is described in the Supporting Information (SI). The ZIF-8 precursor was activated at 100 °C under vacuum for 2 h prior to characterization. Guest molecule diffusion in the ZIF-8 precursor and thermally modified ZIFs was studied with pressure-decay sorption at 35 °C using sulfur hexafluoride (SF_6; 5.5 Å), *n*-butane (*n*-C_4H_{10}; 4.3 Å), and *iso*-butane (*iso*-C_4H_{10}; 5.0 Å) as guest molecules. To ensure reliable and convenient diffusion measurements, two ZIF-8 precursor samples (Figure S1 in the SI) with average equivalent diameters of 92 nm[25] and 15.8 μm[5] were synthesized. The 92 nm ZIF-8 sample was used to prepare thermally modified ZIFs for SF_6 and *iso*-C_4H_{10} diffusion measurements, while the 15.8 μm sample was used to prepare thermally modified ZIFs for *n*-C_4H_{10} diffusion measurements.

In addition to TGA (Figure S2 in the SI) and diffusion measurements, thermally modified ZIFs were characterized by scanning electron microscopy (SEM), PXRD, as well as surface area and porosity analysis (N_2 physisorption at 77K). SEM imaging (Figure S1 in the SI) showed no changes in either the crystal size or shape after thermal treatment. This is reasonable because the overall crystal integrity should be maintained if methyl group dissociation is the major structural change. PXRD results (Figure S3 in the SI) suggested that the long-range crystal orders were well-maintained after thermal treatment. N_2 physisorption results (Figure S4 in the SI) are, in general, consistent with the observations by Gadipelli and co-workers[22] that both the surface area and porosity were reduced with increasing thermal treatment temperature. For the ZIF thermally modified at 500 °C for 2 h, the Brunauer−Emmett−Teller (BET) surface area and micropore volume were respectively reduced by 15 and 30% compared with the ZIF-8 precursor.

The effect of thermal treatment temperature on guest molecule (SF_6, *n*-C_4H_{10}, and *iso*-C_4H_{10}) diffusion is shown in Figure 1. The diffusivity essentially stayed constant for ZIFs thermally treated below 300 °C, suggesting that the ZIF structure was intact and the effective aperture size was unchanged. This is in agreement with TGA−MS results that minimal gas species were detected when heated below 300 °C. A slight increase in the diffusivity was observed as the thermal treatment temperature continued to increase to 400 °C, which is again in excellent consistency with TGA−MS results in which the onset of C−C bond cleavage and methyl group dissociation occurs at 350−400 °C. As the thermal treatment temperature further increased to 500 °C, the thermally modified ZIFs showed more rapidly increased guest molecule diffusivity because of the aggressive loss of methyl groups above 400 °C.

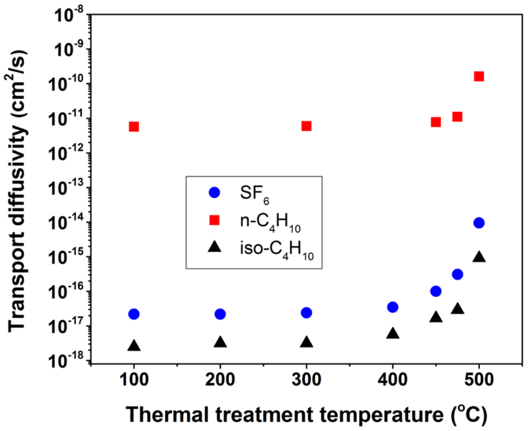


Figure 1. Guest molecule (SF_6, *n*-C_4H_{10}, and *iso*-C_4H_{10}) transport diffusivity data in the ZIF-8 precursor (activated at 100 °C) and ZIFs thermally modified at 200, 300, 400, 450, 475, and 500 °C.

As methyl groups dissociate, MeIM linkers controlling the ZIF's six-ring aperture size are reduced to smaller imidazoles, and as a result, the aperture is enlarged. The degree of aperture enlargement, obviously, is determined by the percentage of dissociated methyl groups. Ideally, maximum aperture enlargement occurs when all methyl groups are removed with all MeIM linkers reduced to imidazole, and the material is changed from $Zn(MeIM)_2$ to $Zn(IM)_2$. Upon a comparison of the ZIF thermally modified at 500 °C and the ZIF-8 precursor, the transport diffusivities of SF_6, *n*-C_4H_{10}, and *iso*-C_4H_{10} increased by 432, 28, and 400 times, respectively. The percentages (θ, Table S1) of methyl groups that dissociate from the ZIF-8 framework for each thermally treated ZIF sample were calculated based on the TGA weight loss (Figure S2) and theoretical weight loss (13.2%) assuming complete methyl group dissociation. Despite being able to retain long-range crystal order, samples thermally modified at 500 °C showed weakened PXRD peaks at higher 2θ angles. This suggested existence of locally disordered pores, which may result in reduced BET surface area and micropore volume (Figure S4). In addition to aperture enlargement as a result of methyl group dissociation, such local disorder may have contributed to changes in guest molecule diffusivities, possibly as a secondary effect. It is worth noting that the 400 times increase in the *iso*-butane diffusivity was caused by dissociation of only 17% of the framework methyl groups. It is interesting to compare the post-synthetic thermal modification (PSTM) method with aluminosilicates extraframework cation exchange. While the PSTM method enlarges the ZIF's aperture by linker size reduction, enlarging aluminosilicate zeolite apertures can be realized by exchanging larger extraframework cations with smaller ones (e.g., Na^+ to Li^+) or replacing monovalent extraframework cations with divalent ones (e.g., Na^+ to Ca^{2+}).[26]

n-Butane diffusivity data and *n*/*iso*-butane diffusion selectivities of the ZIF-8 precursor and ZIF samples thermally modified at 450, 475, and 500 °C are plotted in Figure 2 with the fraction of thermally removed methyl groups. Figure 2 shows that the PSTM technique can be conveniently used to tailor ZIFs' transport properties. The *n*-butane diffusivity was substantially increased with removal of framework methyl groups. For the ZIF sample thermally treated at 500 °C (θ = 17 wt %), the *n*-butane diffusivity increased by 28 times (from 5.7×10^{-12} to 1.6×10^{-10} cm^2/s) compared with that of the ZIF-8 precursor. While the *n*/*iso*-butane selectivity was reduced (from 2.5×10^6

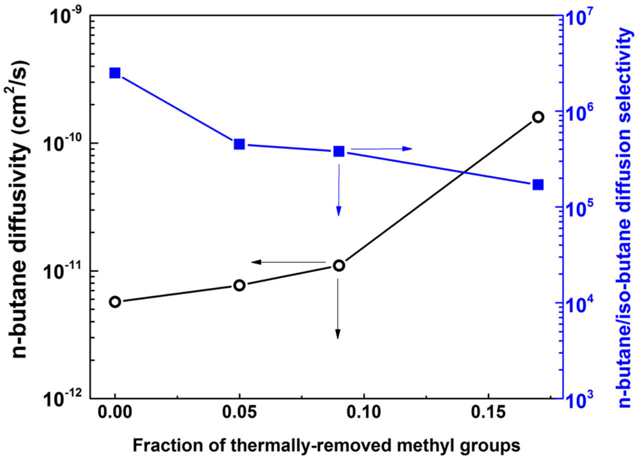


Figure 2. Effect of thermally induced methyl group removal on ZIF-8's *n*-butane diffusivity and *n*/*iso*-butane diffusion selectivity.

to 1.7 × 10^5) as a result of enlarged apertures and reduced molecular sieving capability, it still remains highly attractive for efficient separation. An additional increase in the *n*-butane diffusivity is expected for samples thermally treated at higher temperature or prolonged time; however, caution is needed because framework decomposition may occur for prolonged heat treatment above 525 °C,[22] which may substantially reduce the material's diffusion selectivity.

The alkylation process is critical to producing high-octane rating stocks for premium gasoline blending. The process produces highly branched alkylates by reacting C_{3-5} olefins with *iso*-butane, which is separated from butane isomerization products (*n*- and *iso*-butane). Butane isomer separation is conventionally realized by highly energy-intensive fractional distillation, and a membrane unit can be used to debottleneck the separation with improved process energy efficiency. Figure 3a shows a simplified flow scheme of alkylation process debottlenecking with membrane separation. Membrane retentate with enriched *iso*-butane is introduced to the distillation column, and membrane permeate with enriched *n*-butane is recycled to the butane isomerization reactor.

Membrane-based butane isomer separation is challenging. Both polymer and zeolite membranes have been considered. While polymer membranes are highly scalable, C_4 hydrocarbon diffusion is slow in glassy polymers, and accordingly permeability is economically unattractive.[28,29] Among several studied zeolitic materials, MFI-type zeolite membranes[30] offered the most promising separation performance with a *n*/*iso*-butane separation factor (at 25 °C) of up to 62. Nevertheless, the high cost of zeolite membrane synthesis and low packing efficiency of the alumina-supported tubular geometry have compromised the scalability of zeolite membranes. On the other hand, hybrid mixed-matrix membranes (Figure 3a) offer excellent balance between separation performance and scalability by dispersing highly selective and permeable molecular sieve particles inside continuous and easily processed polymer matrices.

Figure 3b compares the estimated *n*/*iso*-butane separation performance of mixed-matrix membranes formed using ZIF-8 and the 500 °C thermally modified ZIF. The permeability and selectivity of mixed-matrix membranes were estimated by the Maxwell model (see the SI). The polymer matrix was 6FDA-DAM[17,28] in both cases, which had an *n*-butane permeability of 0.5 Barrer (Table S2) and an *n*/*iso*-butane ideal selectivity of 21 at 35 °C. The results suggest that the PSTM technique can be a very powerful tool to create structurally modified ZIFs for advanced membrane separations. Because of ZIF-8's unattractive *n*-butane permeability (0.12 Barrer), *n*/*iso*-butane separation performance of ZIF-8/6FDA-DAM mixed-matrix membranes is expected to be poor. At 45 vol % ZIF-8 loading, calculations (see the SI) predicted 40% reduction in *n*-butane permeability and only slightly (30%) increased *n*/*iso*-butane permselectivity for ZIF-8/6FDA-DAM mixed-matrix membranes over the pure 6FDA-DAM matrix. On the contrary, substantial increases in both the *n*-butane permeability and *n*/*iso*-butane permselectivity are expected for mixed-matrix membranes formed using the thermally modified ZIF (*n*-butane permeability ∼ 2.9 Barrer; Table S2). At 45 vol % ZIF loading, the mixed-matrix membrane *n*-butane permeability is enhanced by more than 100% and the *n*/*iso*-butane permselectivity is remarkably increased to 102, which is ∼400% higher than that of the polymer matrix 6FDA-DAM.

It should be noted that the estimated mixed-matrix membrane permeation properties in Figure 3b were based on single-component diffusion measurements. Reduced ZIF *n*-butane diffusivity and *n*/*iso*-butane diffusion selectivity are expected under binary *n*/*iso*-butane mixture sorption because of competitive diffusion between *n*- and *iso*-butane molecules. Accordingly, the mixed-matrix membrane *n*-butane perme-

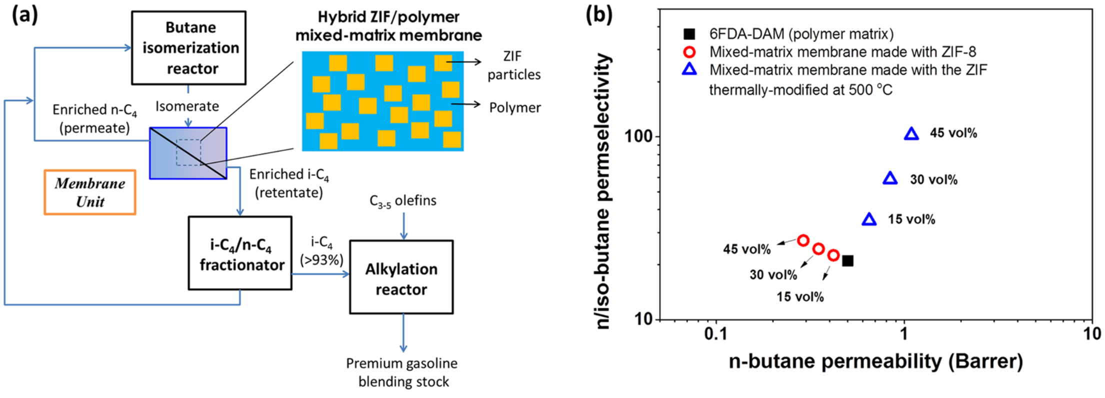


Figure 3. (a) Simplified flow scheme of alkylation process debottlenecking with membrane separation[27] and structural illustration of a hybrid ZIF/polymer mixed-matrix membrane. (b) Comparing the estimated *n*-butane permeability and *n*/*iso*-butane permselectivity (at 35 °C) of mixed-matrix membranes prepared using ZIF-8 and the ZIF thermally modified at 500 °C.

ability and n/*iso*-butane separation factor are expected to be lower under n/*iso*-butane mixture membrane permeation than the numbers shown in Figure 3b. Additionally, it is worth noting that the purpose of Figure 3b is to demonstrate the usefulness of the PSTM technique to tailor ZIF's transport properties for membrane separation applications. The reliability of estimated mixed-matrix membrane n/*iso*-butane separation performance in Figure 3b is subject to uncertainties of diffusivity measurements (pressure-decay sorption) and limitations of the idealized Maxwell model at higher particle loadings.

In conclusion, we have reported a facile PSTM technique that offers great opportunities to develop ZIFs with tailorable transport properties. Guest molecule (SF_6, n-C_4H_{10}, and *iso*-C_4H_{10}) diffusivities in thermally modified ZIFs were enhanced with increasing thermal treatment temperature (400−500 °C) because of progressive methyl group dissociation and, consequently, enlarged aperture. The ZIF thermally modified at 500 °C showed 28 times increase in the n-butane diffusivity, with the n/*iso*-butane diffusion selectivity (1.7×10^5) remaining attractive. The thermally modified ZIF is expected to substantially increase n/*iso*-butane separation performance of hybrid ZIF/polymer mixed-matrix membranes, which can be potentially used to debottleneck refinery alkylation processes. While the example is given by tailoring ZIF-8's transport properties with controllable removal of methyl groups, we expect that the PSTM approach discussed in this study is generalizable. It may be potentially extended to other ZIF or MOF precursors constructed by ligands comprising thermally removable groups.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b07769.

> Synthesis of ZIF-8 precursor samples, formation of thermally modified ZIF samples, and characterization (diffusion measurements, SEM, TGA, PXRD, and N_2 physisorption) (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: wjk@chbe.gatech.edu.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

W.J.K. acknowledges financial support from Roberto C. Goizueta, Chair for Excellence in Chemical Engineering, King Abdullah University of Science and Technology (Award KUS-I1-011-21), and Office of Basic Energy Science of the U.S. Department of Energy (Grant DE-FG02-04ER15510).

■ REFERENCES

(1) Phan, A.; Doonan, C. J.; Uribe-Romo, F. J.; Knobler, C. B.; O'Keeffe, M.; Yaghi, O. M. Synthesis, Structure, and Carbon Dioxide Capture Properties of Zeolitic Imidazolate Frameworks. *Acc. Chem. Res.* **2010**, *43*, 58−67.

(2) Ryder, M. R.; Civalleri, B.; Bennett, T. D.; Henke, S.; Rudić, S.; Cinque, G.; Fernandez-Alonso, F.; Tan, J.-C. Identifying the Role of Terahertz Vibrations in Metal-Organic Frameworks: From Gate-Opening Phenomenon to Shear-Driven Structural Destabilization. *Phys. Rev. Lett.* **2014**, *113*, 215502.

(3) Fairen-Jimenez, D.; Moggach, S. A.; Wharmby, M. T.; Wright, P. A.; Parsons, S.; Duren, T. Opening the Gate: Framework Flexibility in ZIF-8 Explored by Experiments and Simulations. *J. Am. Chem. Soc.* **2011**, *133*, 8900−8902.

(4) Zhang, K.; Lively, R. P.; Zhang, C.; Chance, R. R.; Koros, W. J.; Sholl, D. S.; Nair, S. Exploring the Framework Hydrophobicity and Flexibility of ZIF-8: From Biofuel Recovery to Hydrocarbon Separations. *J. Phys. Chem. Lett.* **2013**, *4*, 3618−3622.

(5) 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.

(6) Bux, H.; Chmelik, C.; van Baten, J. M.; Krishna, R.; Caro, J. Novel MOF-Membrane for Molecular Sieving Predicted by IR-Diffusion Studies and Molecular Modeling. *Adv. Mater.* **2010**, *22*, 4741−4743.

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

(8) Pimentel, B. R.; Parulkar, A.; Zhou, E.-k.; Brunelli, N. A.; Lively, R. P. Zeolitic Imidazolate Frameworks: Next-Generation Materials for Energy-Efficient Gas Separations. *ChemSusChem* **2014**, *7*, 3202−3240.

(9) Caro, J. Are MOF Membranes Better in Gas Separation Than Those Made of Zeolites? *Curr. Opin. Chem. Eng.* **2011**, *1*, 77−83.

(10) Zhang, C.; Koros, W. J. Zeolitic Imidazolate Framework-*Enabled* Membranes: Challenges and Opportunities. *J. Phys. Chem. Lett.* **2015**, *6*, 3841−3849.

(11) Hara, N.; Yoshimune, M.; Negishi, H.; Haraya, K.; Hara, S.; Yamaguchi, T. Diffusive Separation of Propylene/Propane with ZIF-8 Membranes. *J. Membr. Sci.* **2014**, *450*, 215−223.

(12) Liu, D.; Ma, X.; Xi, H.; Lin, Y. S. Gas Transport Properties and Propylene/Propane Separation Characteristics of ZIF-8 Membranes. *J. Membr. Sci.* **2014**, *451*, 85−93.

(13) Pan, Y.; Liu, W.; Zhao, Y.; Wang, C.; Lai, Z. Improved ZIF-8 Membrane: Effect of Activation Procedure and Determination of Diffusivities of Light Hydrocarbons. *J. Membr. Sci.* **2015**, *493*, 88−96.

(14) 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.

(15) 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.

(16) 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.

(17) Zhang, C.; Dai, Y.; Johnson, J. R.; Karvan, O.; Koros, W. J. High Performance ZIF-8/6FDA-DAM Mixed Matrix Membrane for Propylene/Propane Separations. *J. Membr. Sci.* **2012**, *389*, 34−42.

(18) Zhang, C.; Zhang, K.; Xu, L.; Labreche, Y.; Kraftschik, B.; Koros, W. J. Highly Scalable ZIF-Based Mixed-Matrix Hollow Fiber Membranes for Advanced Hydrocarbon Separations. *AIChE J.* **2014**, *60*, 2625−2635.

(19) Eum, K.; Jayachandrababu, K. C.; Rashidi, F.; Zhang, K.; Leisen, J.; Graham, S.; Lively, R. P.; Chance, R. R.; Sholl, D. S.; Jones, C. W.; Nair, S. Highly Tunable Molecular Sieving and Adsorption Properties of Mixed-Linker Zeolitic Imidazolate Frameworks. *J. Am. Chem. Soc.* **2015**, *137*, 4191−4197.

(20) Klemola, K. T.; Ilme, J. K. Distillation Efficiencies of an Industrial-Scale I-Butane/N-Butane Fractionator. *Ind. Eng. Chem. Res.* **1996**, *35*, 4579−4586.

(21) Shekhah, O.; Swaidan, R.; Belmabkhout, Y.; du Plessis, M.; Jacobs, T.; Barbour, L. J.; Pinnau, I.; Eddaoudi, M. The Liquid Phase Epitaxy Approach for the Successful Construction of Ultra-Thin and

Defect-Free ZIF-8 Membranes: Pure and Mixed Gas Transport Study. *Chem. Commun.* **2014**, *50*, 2089−2092.

(22) Gadipelli, S.; Travis, W.; Zhou, W.; Guo, Z. A Thermally Derived and Optimized Structure from ZIF-8 with Giant Enhancement in CO_2 Uptake. *Energy Environ. Sci.* **2014**, *7*, 2232−2238.

(23) 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.

(24) Karagiaridi, O.; Lalonde, M. B.; Bury, W.; Sarjeant, A. A.; Farha, O. K.; Hupp, J. T. Opening ZIF-8: A Catalytically Active Zeolitic Imidazolate Framework of Sodalite Topology with Unsubstituted Linkers. *J. Am. Chem. Soc.* **2012**, *134*, 18790−18796.

(25) Zhang, C.; Gee, J. A.; Sholl, D. S.; Lively, R. P. Crystal-Size-Dependent Structural Transitions in Nanoporous Crystals: Adsorption-Induced Transitions in ZIF-8. *J. Phys. Chem. C* **2014**, *118*, 20727−20733.

(26) Padin, J.; Rege, S. U.; Yang, R. T.; Cheng, L. S. Molecular Sieve Sorbents for Kinetic Separation of Propane/Propylene. *Chem. Eng. Sci.* **2000**, *55*, 4525−4535.

(27) Esekhile, O. Mixed Matrix Membranes for Mixture Gas Separation of Butane Isomers. Ph.D. Dissertation, Georgia Institute of Technology, Atlanta, GA, 2011.

(28) Esekhile, O.; Qiu, W. L.; Koros, W. J. Permeation of Butane Isomers through 6FDA-DAM Dense Films. *J. Polym. Sci., Part B: Polym. Phys.* **2011**, *49*, 1605−1620.

(29) Liu, J.; Bae, T.-H.; Qiu, W.; Husain, S.; Nair, S.; Jones, C. W.; Chance, R. R.; Koros, W. J. Butane Isomer Transport Properties of 6FDA−DAM and MFI−6FDA−DAM Mixed Matrix Membranes. *J. Membr. Sci.* **2009**, *343*, 157−163.

(30) Agrawal, K. V.; Topuz, B.; Pham, T. C. T.; Nguyen, T. H.; Sauer, N.; Rangnekar, N.; Zhang, H.; Narasimharao, K.; Basahel, S. N.; Francis, L. F.; Macosko, C. W.; Al-Thabaiti, S.; Tsapatsis, M.; Yoon, K. B. Oriented MFI Membranes by Gel-Less Secondary Growth of Sub-100 nm MFI-Nanosheet Seed Layers. *Adv. Mater.* **2015**, *27*, 3243−3249.

DOI: 10.1021/acsami.5b07769