Exploring the Framework Hydrophobicity and Flexibility of ZIF-8: From Biofuel Recovery to Hydrocarbon Separations

7 AUTHORS, INCLUDING:

Ke Zhang
Aramco Services Company
27 PUBLICATIONS   **526** CITATIONS

SEE PROFILE

Chen Zhang
Georgia Institute of Technology
16 PUBLICATIONS   **384** CITATIONS

SEE PROFILE

Ronald R Chance
Georgia Institute of Technology
139 PUBLICATIONS   **8,784** CITATIONS

SEE PROFILE

William Koros
Georgia Institute of Technology
252 PUBLICATIONS   **8,111** CITATIONS

SEE PROFILE

Exploring the Framework Hydrophobicity and Flexibility of ZIF-8: From Biofuel Recovery to Hydrocarbon Separations

Ke Zhang,[†] Ryan P. Lively,[†,‡] Chen Zhang,[†] Ronald R. Chance,[†,‡] William J. Koros,[†] David S. Sholl,[†] and Sankar Nair*,[†]

[†]School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States
[‡]Algenol Biofuels, 28100 Bonita Grande Drive, Bonita Springs, Florida 34315, United States

S Supporting Information

ABSTRACT: The framework hydrophobicity and flexibility of ZIF-8 are investigated by a detailed adsorption and diffusion study of a series of probe molecules including ethanol, 1-butanol, water, hexane isomers, xylene isomers, and 1,2,4-trimethylbenzene. The prospects for using ZIF-8 in biofuel recovery and hydrocarbon separations are discussed in terms of adsorption or kinetic selectivities. ZIF-8 shows extremely low water vapor uptakes and is especially suitable for vapor phase butanol-based biofuel recovery. The extraordinary framework flexibility of ZIF-8 is demonstrated by the adsorption of hydrocarbon molecules that are much larger than its nominal pore size, such as *m*-xylene, *o*-xylene and 1,2,4-trimethylbenzene. The calculation of corrected diffusion coefficients reveals an interesting spectrum of promising kinetic hydrocarbon separations by ZIF-8. These findings confirm that a molecular sieving effect tends to occur in the sorbate molecular size range of 4−6 Å rather than around the nominal ZIF-8 pore size of 3.4 Å, due to its surprising framework flexibility.

SECTION: Surfaces, Interfaces, Porous Materials, and Catalysis
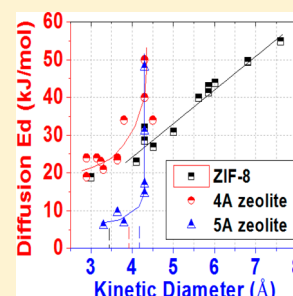
Zeolitic imidazolate frameworks (ZIFs) are a subset of metal−organic frameworks (MOFs) with three-dimensional structures connected by metal centers and organic linkers based upon imidazolate (Im) species. ZIFs are known to have some of the highest chemical and thermal stabilities among MOF materials. During the past decade, the rational synthesis of more than 90 ZIF structures has been accomplished, including crystal topologies not yet realized in the synthesis of zeolites.[1−4] ZIF frameworks can be inherently hydrophobic if the Im linkers do not contain hydrophilic functional groups.[5,6] Moreover, ZIF structures are shown to be flexible enough to allow the passage of molecules larger than their crystallographically derived aperture size.[7] ZIF-8 (Zn(MeIM)$_2$, MeIM = 2-methylimidazole) is a well-known ZIF that has been extensively studied as an adsorbent or a membrane since its nominal aperture size (~3.4 Å) is in the range of the effective molecular sizes of many gases of interest.[8−11] Unfortunately, contrary to zeolites with relatively rigid structures, there is convincing evidence that the aperture of ZIF-8 is extremely flexible, and there exists no sharp molecular sieving "cut-off" at 3.4 Å.[12−14] The large cages of ZIF-8 have been shown to be accessible to a series of hydrocarbon molecules with kinetic diameters of 4.3−5.85 Å that are significantly larger than its nominal crystallographic aperture size.[15−18] This structural flexibility opens up new opportunities for ZIF-8 as a potentially effective material with unique separation capabilities, but also creates an uncertainty regarding the range of molecules that can be adsorptively or kinetically separated with ZIF-8. An adsorption and diffusion study of molecules up to C$_4$ hydrocarbons in ZIF-8 has been recently reported, whereas

information on higher-molecular weight penetrants in ZIF-8 is not available.[7]

To elucidate the above issue, here we provide a comprehensive characterization of the molecular adsorption and diffusion properties of a large collection of molecules with a large size range (3.0−7.6 Å) in ZIF-8. In particular, we have conducted a detailed vapor-phase adsorption and diffusion study of H$_2$O, ethanol, 1-butanol, *n*-hexane (*n*C$_6$), 3-methylpentane (3MP), 2,3-dimethylbutane (23DMB), *n*-heptane (*n*C$_7$), benzene, *ortho*-xylene (*o*X), *meta*-xylene (*m*X), *para*-xylene (*p*X), ethylbenzene (EB), and 1,2,4-trimethylbenzene (124-TMB) in ZIF-8. The transport diffusivities are obtained by fitting the kinetic uptake curves in synthesized ZIF-8 crystals with transient diffusion models, and are then corrected by a thermodynamic factor to estimate the corrected diffusivities that are essentially not subject to adsorbate loading effects.[19,20] Our experimental data are discussed in relation to some valuable separation cases such as biofuel recovery, separation of C$_6$ paraffins, and separation of xylene isomers. The diffusion activation energy is correlated with kinetic diameters of probe molecules.

Due to its relatively well-established synthesis chemistry with the fabrication of controllable crystal sizes, ZIF-8 is an ideal candidate for this diffusion study using kinetic uptake methods. As demonstrated in this work, the molecular diffusion

coefficients vary over 11 orders of magnitude, and hence it was impractical to measure diffusivities of all the studied molecules in ZIF-8 samples with a single crystal size. Thus, ZIF-8 crystals with average diameter of 50 nm, 16 μm, and 324 μm were synthesized for adsorption and kinetic measurements of different adsorbates according to their molecular sizes. Detailed synthesis procedures, powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), N_2 physisorption results, crystal size analysis, diffusivity calculation, and detailed diffusivity data and plot can be found in the Supporting Information. SEM images (Supporting Information) show rhombic dodecahedron-shaped microcrystals and spherical-shaped nanocrystals. For molecules with kinetic diameters above 5.0 Å, only the 50 nm ZIF-8 crystals were used to obtain reasonably fast uptake curves for the estimation of transport diffusivities. A VTI-SA vapor sorption analyzer (TA Instruments) was used for uptake measurements. Adsorption equilibrium was assumed to be achieved if the mass changes were less than 0.003 wt % in a 5-min interval.

The vapor-phase adsorption isotherms of water, ethanol and 1-butanol at 50 °C are summarized in Figure 1. For water
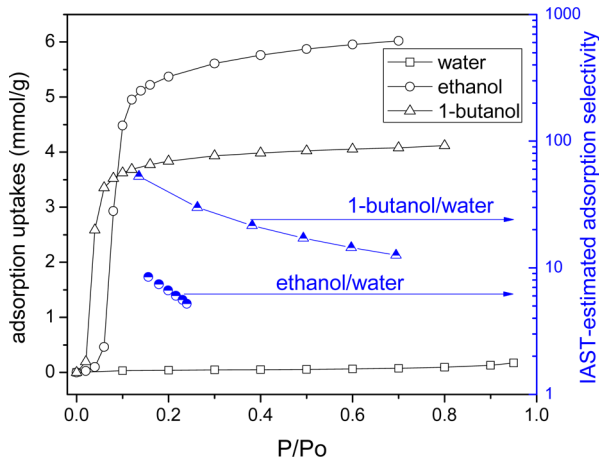

Figure 1. Single-component adsorption isotherms of water, ethanol and 1-butanol, and IAST-estimated alcohol/water adsorption selectivities in ZIF-8, at 50 °C.

adsorption, the equilibrium uptakes are very low even at the highest P/P_o of 0.95 (~0.175 mmol/g), indicating the strong hydrophobicity of ZIF-8. The hydrophobicity of ZIF-8 is comparable with the fluoride-mediated MFI silicalite-1 in terms of equilibrium water uptakes.[21,22] This characteristic derives from the methyl-functionalized Im linkers in ZIF-8 and the coordinative saturation of the metal sites. The framework hydrophobicity is also evidenced by the significant effect of outer surface area on the water uptakes (due to the existence of the hydrophilic −N−H functionality at the crystal surfaces), even though ZIF-8 is a microporous material with BET surface area >1500 m²/g.[6] For alcohol adsorption, the isotherms usually exhibit an initial step before cage-filling occurs, suggesting that ZIF-8 is only capable of adsorbing alcohols at activities in the cage-filling region. The initial low-uptake region moves to smaller P/P_o values for 1-butanol adsorption, which creates a unique opportunity for butanol-based biofuel recovery by ZIF-8. Since diffusion in ZIF-8 favors the smaller water molecules over the alcohols, the potential of using ZIF-8 in biofuel recovery (such as ethanol/water and butanol/water separation) depends solely on the adsorption selectivity. The

alcohol/water adsorption selectivity is defined as the alcohol:-water concentration ratio in the adsorbed phase over the same concentration ratio in the vapor phase. The vapor-phase concentration ratio was obtained from the partial vapor pressures in equilibrium with the liquid alcohol/water feed compositions. The concentration ratio in the adsorbed phase was estimated by the Ideal Adsorbed Solution Theory (IAST),[23] using the single-component adsorption isotherms. IAST can provide an accurate prediction of alcohol uptakes, as well as a reasonable estimation of water uptakes from water vapor feeds near the saturation vapor pressure.[24,25] Figure 1 reveals that ZIF-8 has promising adsorption selectivity for both ethanol- and butanol-based biofuel purifications. ZIF-8 shows exceptionally high adsorption selectivity for 1-butanol recovery. For example, the equilibrium vapor-phase concentration for a 0.25 mol % liquid 1-butanol feed is approximately 4.5 mol % 1-butanol and 95.5 mol % water at 50 °C. An adsorption selectivity of 53 indicates a concentrated adsorbed phase of 71.4 mol % 1-butanol and 28.6 mol % water. The unique capability of ZIF-8 for butanol-based biofuel recovery has also been demonstrated in a ZIF-8/polymethylphenylsiloxane (PMPS) mixed-matrix membrane operated in pervaporation mode.[26]

From Figure 1, it is clear that ethanol and 1-butanol readily access the pore volume of ZIF-8 due to the structural flexibility of its limiting apertures. To further explore this issue, we studied systematically the adsorption and diffusion of a series of C_6-C_9 hydrocarbons. Figure 2 shows the adsorption isotherms
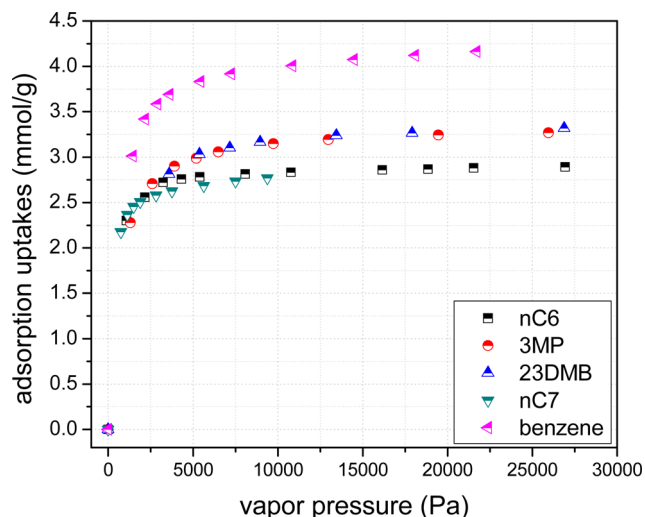

Figure 2. Single-component adsorption isotherms of nC_6, 3MP, 23DMB, nC7, and benzene in ZIF-8 at 50 °C.

of nC_6, nC_7, 3MP, 23DMB, and benzene. All these molecules are confirmed to access the ZIF-8 cages, indicating that the limiting aperture size of ZIF-8 is at least larger than the size of benzene molecules. The adsorption of nC_6 and nC_7 in ZIF-8 is anticipated, considering their kinetic diameters ~4.3 Å, and was also reported previously for nC_6.[15,18] Since the cage-filling phenomenon also occurs for 3MP and 23DMB in ZIF-8, there is essentially no equilibrium adsorption selectivity for C_6 paraffins. Interestingly, the branched C_6 alkanes exhibit slightly higher adsorption than nC_6 in ZIF-8, which is consistent with molecular simulations in which a no-cage-blocking strategy was applied.[27] Since ZIF-8 has large cages of size 11.6 Å, the entropic effect favoring branched isomers would operate when
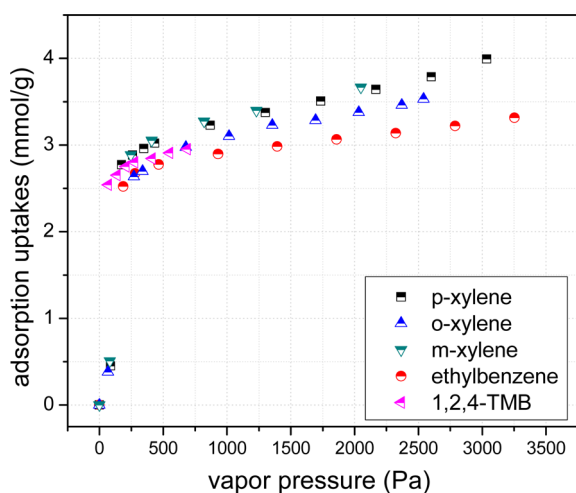
Figure 3. Single-component adsorption isotherms of *p*X, *m*X, *o*X, EB, and 124TMB in ZIF-8 at 50 °C.
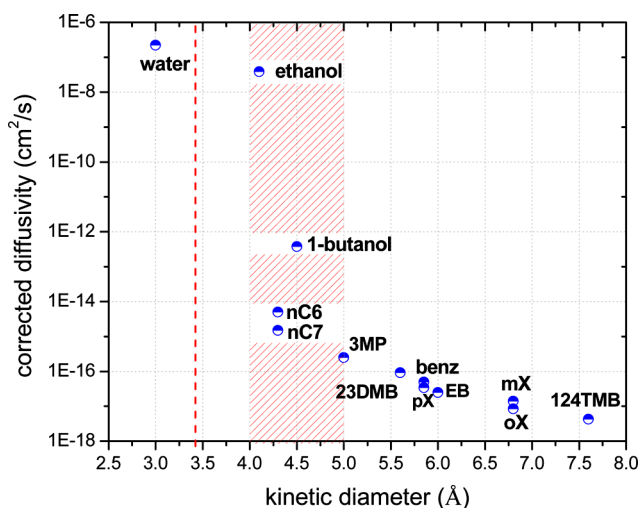

Figure 4. Corrected diffusivities in ZIF-8 at 50 °C versus kinetic diameters of probe molecules. Red dashed line: XRD-derived aperture size of ZIF-8.

cage-filling conditions are approached, as also observed in large-pore zeolites.[27]

The adsorption isotherms of *p*X, *m*X, *o*X, EB, and 124-TMB are illustrated in Figure 3. It is very interesting to note that all of these molecules adsorb in ZIF-8, thus pushing the 'limiting' aperture size of ZIF-8 above the kinetic diameter of 124TMB (7.6 Å). The limiting aperture size of ZIF-8 was previously estimated to be around 5.8 Å as evidenced by the uptakes of 23-DMB and *p*X and exclusion of 22-DMB, *m*X and *o*X.[16−18,27] In this work, we show clearly that even *m*X, *o*X and 124TMB can be adsorbed into the cages of ZIF-8, although with much lower diffusivities. We are able to observe these processes because of our use of appropriately sized ZIF-8 nanocrystals and the sufficient equilibration time. For molecules larger than 5.8 Å, the diffusion becomes extraordinarily slow. For example, more than two weeks of equilibration time was needed for 124TMB at a relative pressure of 0.04 at 50 °C in 50 nm ZIF-8 crystals. In the literature, submicrometer ZIF-8 crystals (several hundred nanometers) are generally used together with a manometric or breakthrough method.[16−18,27] According to our study using nanosized crystals, it is impractical to measure equilibrium uptakes for adsorbates larger than 5.8 Å using larger ZIF-8 crystals by either manometric or breakthrough methods, due to the extremely slow diffusion. Figure 3 also reveals that there is no ideal (single-component) adsorption selectivity for xylene separation in ZIF-8, similar to the case of C₆ paraffins.

While ZIF-8 shows little ideal adsorption selectivity for hydrocarbon separations near cage-filling conditions, the adsorbate diffusion coefficients can differ tremendously with slight changes of molecular dimensions. Figure 4 shows a relationship of the corrected diffusivity in ZIF-8 at 50 °C versus adsorbate kinetic diameters. See Supporting Information for details of how the corrected diffusivities were obtained from the uptake data. The kinetic diameters are used for all of the adsorbates in Figure 4. It is seen that the corrected diffusivity drops over 11 orders of magnitude from water (3.0 Å) to 124-TMB (7.6 Å). In the range of 4.0−5.0 Å, the corrected diffusivity drops 8 orders of magnitude. Therefore, ZIF-8 is most effective within this size range to provide kinetic separations, such as the separation of propylene/propane, *n*-butane/*iso*-butane and *iso*-butene/*iso*-butane.[7,28] When the probe molecules are larger than 5.0 Å, the corrected diffusivities decrease significantly due to strong diffusion limitations.

However, it is interesting that ZIF-8 can still exhibit diffusion selectivity for certain hydrocarbon separations owing to its extraordinary framework flexibility. For example, the diffusion selectivities for *n*C6/3MP, *n*C₆/23DMB and 3MP/23DMB are 20, 54, and 3 respectively. In C₆ paraffins, the branched isomers have higher octane numbers. The current industrial adsorbent for this separation is zeolite 5A, which only adsorbs linear alkanes and rejects both mono- and dibranched isomers.[29,30] Here, ZIF-8 is shown to be capable of kinetically separating not only branched alkanes from linear hexane, but also dibranched alkanes from monobranched isomers. This unique property renders ZIF-8 a potentially superior substitute to zeolite 5A in C₆ paraffin isomer separation. Another example is the case of xylene separation. Since *o*X and *m*X are larger than *p*X molecules, it is found here that ZIF-8 shows a diffusion selectivity of 4.0 (2.4) for *p*X/*o*X (*p*X/*m*X). This is a rare case that a MOF material can exhibit *p*X-selective behavior over *o*X and *m*X, considering that *p*X has the lowest boiling point and lowest dipole moment among the xylene isomers.[31] MOF materials tend to exhibit electrostatics-based *o*X selectivity, due to the relatively strong dipole moment of *o*X. In Figure 4, the general trend of decreasing corrected diffusivity with increasing kinetic diameter is followed, with the exception of *n*C₆ and *n*C₇ with kinetic diameters of 4.3 Å. Also, 1-butanol (4.5 Å) exhibits a higher diffusivity than *n*C₆ and *n*C₇. We attribute this to the obvious inability of the kinetic diameters to describe the differences in the interactions of the linear paraffins with the ZIF-8 framework.

The relationship between the diffusion activation energy (E_d) and kinetic diameter is shown in Figure 5 (also see Figure S4 and Table S2 in the Supporting Information for complete details of the measured diffusivities and fitted activation energies). The E_d values correlate directly with kinetic diameters of guest molecules over a very wide range of corrected diffusivities. Ruthven[32] found that the E_d in zeolites 4A and 5A correlates with the van der Waals diameters of the probe molecules. However, this finding was limited mainly to linear hydrocarbons and small gas molecules. For larger species with aliphatic and aromatic isomers, the present study strongly suggests that kinetic diameters should be applied to correlate E_d, since van der Waals diameters are problematic in
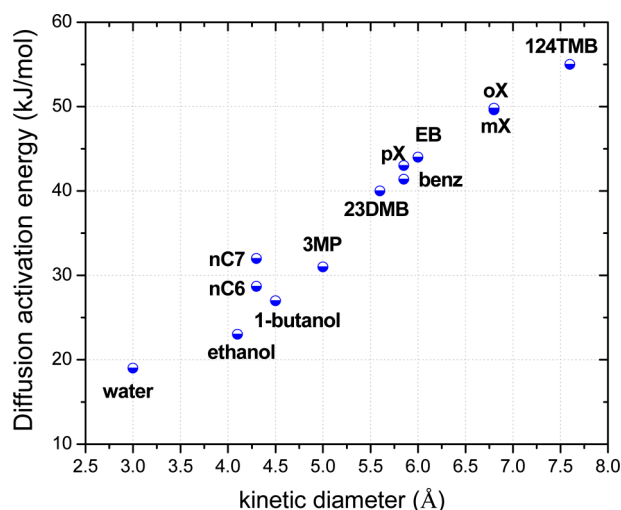
Figure 5. Diffusion activation energy versus kinetic diameters of probe molecules in ZIF-8.

differentiating isomers. The diffusion activation energies are also indicative of the large structural flexibility of ZIF-8 as compared to zeolites 4A and 5A. The diffusion activation energies in zeolites 4A and 5A increase steeply beyond a molecular size of 4 Å, whereas they show a remarkably linear behavior with increasing kinetic diameter in ZIF-8 (see Figure S5, Supporting Information for a graphical comparison). Note that the nominal aperture size of ZIF-8 (3.4 Å) is smaller than the effective aperture sizes of both zeolites 4A (3.8 Å) and 5A (4.3 Å). Therefore, the framework of ZIF-8 is much more flexible than those of similar small-pore zeolites.

In summary, this work demonstrates that ZIF-8 can provide unique separation performance for both biofuel recovery and hydrocarbon separations. Surprisingly, ZIF-8 can adsorb mX, oX, and even 124-TMB molecules to cage-filling levels, indicating a much larger limiting aperture size than any experimental or simulation data reported previously. Moreover, the drastic changes in corrected diffusivities in the molecular size range of 4.0−6.0 Å, especially within 4.0−5.0 Å, reveals a dominant kinetic separation mechanism for almost all hydrocarbon separations that ZIF-8 offers. Indeed, we confirmed the diffusion selectivity for C_6 paraffins (branched over linear; dibranched over monobranched) and xylene separations (pX/oX and pX/mX). Together with the previously identified kinetic separation of C_3H_6/C_3H_8, n-C_4H_{10}/i-C_4H_{10} and i-C_4H_8/i-C_4H_{10} in ZIF-8, these findings constitute a spectrum of kinetic hydrocarbon separations by ZIF-8, deriving from its extraordinary structural flexibility. On the other hand, ZIF-8 may also be a promising alcohol adsorbent in biofuel purification due to its framework hydrophobicity. Contrary to the case of hydrocarbon separations, it is the adsorption selectivity that determines the alcohol recovery efficiency of ZIF-8. The adsorption selectivity is also dependent on the feed concentration, as seen in the typical two-step alcohol isotherms observed here. ZIF-8 is found to be specifically suitable for vapor-phase butanol (rather than ethanol) biofuel recovery. The above interesting separation properties of ZIF-8 indicate that they are potentially attractive alternatives to zeolites as thermodynamically or kinetically selective adsorbents, as well as candidates for permselective membranes for a broad range of separations.

■ ASSOCIATED CONTENT

⑤ Supporting Information

Details of synthesis and characterization of ZIF-8 crystals (SEM, XRD, TGA, crystal size distribution analysis, N_2 physisorption), calculation of transport and corrected diffusivities, detailed diffusivity data in ZIF-8, and comparison with zeolites 4A and 5A. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: sankar.nair@chbe.gatech.edu.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ 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* (1), 58−67.

(2) Banerjee, R.; Phan, A.; Wang, B.; Knobler, C.; Furukawa, H.; O'Keeffe, M.; Yaghi, O. M. High-Throughput Synthesis of Zeolitic Imidazolate Frameworks and Application to CO_2 Capture. *Science* **2008**, *319* (5865), 939−943.

(3) 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* (27), 10186−10191.

(4) He, Y.; Zhou, W.; Krishna, R.; Chen, B. Microporous Metal-Organic Frameworks for Storage and Separation of Small Hydrocarbons. *Chem. Commun.* **2012**, *48* (97), 11813−11831.

(5) Zhang, K.; Lively, R. P.; Dose, M. E.; Brown, A. J.; Zhang, C.; Chung, J.; Nair, S.; Koros, W. J.; Chance, R. R. Alcohol and Water Adsorption in Zeolitic Imidazolate Frameworks. *Chem. Commun.* **2013**, *49*, 3245−3247.

(6) Zhang, K.; Lively, R. P.; Zhang, C.; Koros, W. J.; Chance, R. R. Investigating the Intrinsic Ethanol/Water Separation Capability of ZIF-8: An Adsorption and Diffusion Study. *J. Phys. Chem. C* **2013**, *117* (14), 7214−7225.

(7) 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* (16), 2130−2134.

(8) Bux, H.; Chmelik, C.; Krishna, R.; Caro, J. Ethene/Ethane Separation by the MOF Membrane ZIF-8: Molecular Correlation of Permeation, Adsorption, Diffusion. *J. Membr. Sci.* **2011**, *369* (1−2), 284−289.

(9) 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* (44), 16000−16001.

(10) Venna, S. R.; Carreon, M. A. Highly Permeable Zeolite Imidazolate Framework-8 Membranes for CO_2/CH_4 Separation. *J. Am. Chem. Soc.* **2010**, *132* (1), 76−78.

(11) Pan, Y.; Lai, Z. Sharp Separation of C_2/C_3 Hydrocarbon Mixtures by Zeolitic Imidazolate Framework-8 (ZIF-8) Membranes Synthesized in Aqueous Solutions. *Chem. Commun.* **2011**, *47* (37), 10275−10277.

(12) 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* (23), 8900−8902.

(13) Moggach, S. A.; Bennett, T. D.; Cheetham, A. K. The Effect of Pressure on ZIF-8: Increasing Pore Size with Pressure and the Formation of a High-Pressure Phase at 1.47 GPa. *Angew. Chem., Int. Ed.* **2009**, *48* (38), 7087−7089.

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

(15) Diestel, L.; Bux, H.; Wachsmuth, D.; Caro, J. Pervaporation Studies of *n*-Hexane, Benzene, Mesitylene and Their Mixtures on Zeolitic Imidazolate Framework-8 Membranes. *Microporous Mesoporous Mater.* **2012**, *164*, 288−293.

(16) Peralta, D.; Chaplais, G.; Paillaud, J.-L.; Simon-Masseron, A.; Barthelet, K.; Pirngruber, G. D. The Separation of Xylene Isomers By ZIF-8: A Demonstration of the Extraordinary Flexibility of the ZIF-8 Framework. *Microporous Mesoporous Mater.* **2013**, *173*, 1−5.

(17) Peralta, D.; Chaplais, G.; Simon-Masseron, A.; Barthelet, K.; Chizallet, C.; Quoineaud, A. A.; Pirngruber, G. D. Comparison of the Behavior of Metal-Organic Frameworks and Zeolites for Hydrocarbon Separations. *J. Am. Chem. Soc.* **2012**, *134* (19), 8115−8126.

(18) Peralta, D.; Chaplais, G.; Simon-Masseron, A.; Barthelet, K.; Pirngruber, G. D. Separation of C-6 Paraffins Using Zeolitic Imidazolate Frameworks: Comparison with Zeolite 5A. *Ind. Eng. Chem. Res.* **2012**, *51* (12), 4692−4702.

(19) Cavalcante, C. L.; Ruthven, D. M. Adsorption of Branched and Cyclic Paraffins in Silicalite. 2. Kinetics. *Ind. Eng. Chem. Res.* **1995**, *34* (1), 185−191.

(20) Ruthven, D. M. *Principles of Adsorption and Adsorption Processes*; John Wiley & Sons, Inc.: New York, 1984.

(21) Zhang, K.; Lively, R. P.; Dose, M. E.; Li, L.; Koros, W. J.; Ruthven, D. M.; McCool, B. A.; Chance, R. R. Diffusion of Water and Ethanol in Silicalite Crystals Synthesized in Fluoride Media. *Microporous Mesoporous Mater.* **2013**, *170*, 259−265.

(22) Zhang, K.; Lively, R. P.; Noel, J. D.; Dose, M. E.; McCool, B. A.; Chance, R. R.; Koros, W. J. Adsorption of Water and Ethanol in MFI-Type Zeolites. *Langmuir* **2012**, *28*, 8664−8673.

(23) Myers, A. L.; Prausnitz, J. M. Thermodynamics of Mixed-Gas Adsorption. *AIChE J.* **1965**, *11* (1), 121−127.

(24) Bai, P.; Tsapatsis, M.; Siepmann, J. I. Multicomponent Adsorption of Alcohols onto Silicalite-1 From Aqueous Solution: Isotherms, Structural Analysis, and Assessment of Ideal Adsorbed Solution Theory. *Langmuir* **2012**, *28* (44), 15566−76.

(25) Krishna, R.; van Baten, J. M. Hydrogen Bonding Effects in Adsorption of Water−Alcohol Mixtures in Zeolites and the Consequences for the Characteristics of the Maxwell−Stefan Diffusivities. *Langmuir* **2010**, *26* (13), 10854−10867.

(26) Liu, X. L.; Li, Y. S.; Zhu, G. Q.; Ban, Y. J.; Xu, L. Y.; Yang, W. S. An Organophilic Pervaporation Membrane Derived from Metal−Organic Framework Nanoparticles for Efficient Recovery of Bio-Alcohols. *Angew. Chem., Int. Ed.* **2011**, *50* (45), 10636−10639.

(27) Ferreira, A. F. P.; Mittelmeijer-Hazeleger, M. C.; Granato, M. A.; Martins, V. F. D.; Rodrigues, A. E.; Rothenberg, G. Sieving Di-Branched from Mono-Branched and Linear Alkanes Using ZIF-8: Experimental Proof and Theoretical Explanation. *Phys. Chem. Chem. Phys.* **2013**, *15* (22), 8795−804.

(28) 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* (30), 10368−10369.

(29) Barcia, P. S.; Silva, J. A. C.; Rodrigues, A. E. Octane Upgrading of C-5/C-6 Light Naphtha by Layered Pressure Swing Adsorption. *Energy Fuels* **2010**, *24*, 5116−5130.

(30) Barcia, P. S.; Silva, J. A. C.; Rodrigues, A. E. Adsorption Dynamics of C-5−C-6 Isomerate Fractions in Zeolite Beta for the Octane Improvement of Gasoline. *Energy Fuels* **2010**, *24*, 1931−1940.

(31) Peralta, D.; Barthelet, K.; Perez-Pellitero, J.; Chizallet, C.; Chaplais, G.; Simon-Masseron, A.; Pirngruber, G. D. Adsorption and Separation of Xylene Isomers: CPO-27-Ni vs HKUST-1 vs NaY. *J. Phys. Chem. C* **2012**, *116* (41), 21844−21855.

(32) Ruthven, D. M. Diffusion in Type A Zeolites: New Insights From Old Data. *Microporous Mesoporous Mater.* **2012**, *162*, 69−79.