Rapid Synthesis of Mixed Linker Zeolitic-Imidazolate Framework Membranes for Tunable Gas Separations

Febrian Hillman,[1] Jordan Brito,[1] and Hae-Kwon Jeong*[1,2]

[1]Artie McFerrin Department of Chemical Engineering and [2]Department of Materials Science and Engineering, Texas A&M University, 3122 TAMU, College Station, Texas 77843-3122, United States.

* Corresponding author: hjeong7@tamu.edu

Separating a crude component into a more valuable purer product is a major part of many industrial chemical plants. Typically these processes utilize distillation, which account to 10 – 15 % of world's energy consumption.[1] One alternative solution that can reduce energy consumption up to 90 % relative to distillation is through membrane separation using porous solid material such as zeolites and metal organic frameworks (MOFs).[2] Zeolitic-imidazolate frameworks (ZIFs),[3] a subclass of MOFs, in particular have attracted many attentions due to their chemical/thermal stabilities, their ultra-microporosities, and high surface area when compared to other MOFs material.[3] ZIFs possess zeolite-like topologies in which the tetrahedral Si or Al and the bridging O in zeolite structure are replaced by transition metals (such as Zn,[3] Co,[4] and Cd[5]) and imidazolate-derived linkers. A common drawback for membrane gas separation is the limited availability of aperture pore size and functionalities of the porous materials. Furthermore, the common approach to fabricate ZIF polycrystalline membranes are typically long requiring up to weeks of synthesis.[6-12] Studies have shown that through mixing metals[13, 14] and linkers,[15, 16] one can continuously tune the MOFs/ZIFs (termed hybrid ZIFs) properties to match with the characteristic of specific gas mixture. However, no study have shown the tuning effect of the hybrid ZIFs grown as polycrystalline membrane.

Here, we plan to present a rapid microwave-assisted in situ synthesis of well-intergrown mixed linker ZIF-7-8 membranes in under ~90 s.[17] ZIF-7-8 consists of Zn^{2+} metal nodes bridged by a mixture of benzimidazolate (bIm, ZIF-7 linker) and 2-methylimidazolate (mIm, ZIF-8 linker) linkers.[16] To the best of our knowledge, this is the fastest synthesis of any polycrystalline MOF membranes reported up to now. Furthermore, the gas separation performances (separation factor and permeance) of hybrid ZIF-7-8 membranes were systematically tuned by varying the bIm-to-mIm ratio incorporated into the framework. This is attributed to the fact that an increase in bulky benzimidazolate linker incorporation reduces the effective aperture size of the hybrid framework, consequently improving the separation factor at the expense of reduction in permeance. The unprecedentedly rapid synthesis of ZIF-7-8 membranes with tunable molecular sieving properties is an important step forward for their practical applications in the separation of gas mixtures of interest.

References:

1. *Materials for Separation Technologies: Energy and Emission Reduction Opportunities*, Oak Ridge National Laboratory, Oak Ridge, TN, 2005.
2. D. S. Sholl and R. P. Lively, *Nature*, 2016, **532**, 435-437.
3. K. S. Park, Z. Ni, A. P. Cote, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe and O. M. Yaghi, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 10186-10191.
4. R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keeffe and O. M. Yaghi, *Science*, 2008, **319**, 939-943.
5. O. Karagiaridi, W. Bury, A. A. Sarjeant, C. L. Stern, O. K. Farha and J. T. Hupp, *Chem. Sci.*, 2012, **3**, 3256-3260.
6. Y. Pan and Z. Lai, *Chem. Comm.*, 2011, **47**, 10275-10277.
7. H. Bux, C. Chmelik, R. Krishna and J. Caro, *Journal of Membrane Science*, 2011, **369**, 284-289.
8. H. Bux, A. Feldhoff, J. Cravillon, M. Wiebcke, Y.-S. Li and J. Caro, *Chem. Mater.*, 2011, **23**, 2262-2269.
9. H. Bux, F. Liang, Y. Li, J. Cravillon, M. Wiebcke and J. Caro, *J. Am. Chem. Soc.*, 2009, **131**, 16000-16001.
10. H. T. Kwon and H.-K. Jeong, *Chem. Comm.*, 2013, **49**, 3854-3856.
11. H. T. Kwon and H.-K. Jeong, *J. Am. Chem. Soc.*, 2013, **135**, 10763-10768.
12. H. T. Kwon, H.-K. Jeong, A. S. Lee, H. S. An and J. S. Lee, *J. Am. Chem. Soc.*, 2015, **137**, 12304-12311.
13. C. Wang, F. Yang, L. Sheng, J. Yu, k. Yao, L. Zhang and Y. Pan, *Chem. Comm.*, 2016, **52**, 12578-12581.
14. G. Kaur, R. K. Rai, D. Tyagi, X. Yao, P.-Z. Li, X.-C. Yang, Y. Zhao, Q. Xu and S. K. Singh, *J. Mater. Chem. A*, 2016, **4**, 14932-14938.
15. K. Eum, K. C. Jayachandrababu, F. Rashidi, K. Zhang, J. Leisen, S. Graham, R. P. Lively, R. R. Chance, D. S. Sholl, C. W. Jones and S. Nair, *J. Am. Chem. Soc.*, 2015, **137**, 4191-4197.
16. J. A. Thompson, C. R. Blad, N. A. Brunelli, M. E. Lydon, R. P. Lively, C. W. Jones and S. Nair, *Chem. Mater.*, 2012, **24**, 1930-1936.
17. F. Hillman, J. Brito and H.-K. Jeong, *ACS Applied Materials & Interfaces*, 2018, **10**, 5586-5593.