Gas Separations in Metal-Organic Frameworks

Jeffrey R. Long*

*Departments of Chemistry and Chemical & Biomolecular Engineering,
University of California, Berkeley*
Materials Sciences Division, Lawrence Berkeley National Laboratory

Owing to their high surface areas, tunable pore dimensions, and adjustable surface functionality, metal-organic frameworks (MOFs) can offer advantages for a variety of gas storage and gas separation applications.   In an effort to help curb greenhouse gas emissions from power plants, we are developing new MOFs for use as solid adsorbents in post- and pre-combustion CO_2 capture, and for the separation of O_2 from air, as required for oxy-fuel combustion.   In particular, MOFs with open metal cation sites or diamine-functionalized surfaces are demonstrated to provide high selectivities and working capacities for the adsorption of CO_2 over N_2 under flue gas conditions.[1]   Multicomponent adsorption measurements further show compounds of the latter type to be effective in the presence of water,[2] while calorimetry and temperature swing cycling data reveal a low regeneration energy compared to aqueous amine solutions.[3] MOFs with open metal sites, such as $Mg_2(dobdc)$ ($dobdc^{4-}$ = 2,5-dioxido-1,4- benzenedicarboxylate), are highly effective in the removal of CO_2 under conditions relevant to H_2 production, including in the presence of CH_4 impurities.[4]   Redox-active Fe^{2+} sites in the isostructural compound $Fe_2(dobdc)$ allow the selective adsorption of O_2 over N_2 via an electron transfer mechanism.[5]   The same material is demonstrated to be effective at 45 °C for the fractionation of mixtures of C1 and C2 hydrocarbons, and for the high-purity separation of ethylene/ethane and propylene/propane mixtures.[6]   Finally, it will be shown that certain structural features possible within MOFs, but not in zeolites, can enable the fractionation of hexane isomers according to the degree of branching or octane number.[7]

References
1. McDonald, T. M.; Lee, W. R.; Mason, J. A.; Wiers, B. M.; Hong, C. S.; Long, J. R. *J. Am. Chem. Soc.* **2012**, *134*, 7056.
2. Mason, J. A.; McDonald, T. M.; Bae, T.-H.; Bachman, J. E.; Sumida, K.; Dutton, J. J.; Kaye, S. S.; Long, J. R. *J. Am. Chem. Soc.* **2015**, *137*, 4787.
3. McDonald, T. M.; Mason, J. A.; Kong, X.; Bloch, E. D.; Gygi, D.; Dani, A.; Crocellà, V.; Giordano, F.; Odoh, S.; Drisdell, W.; Vlaisavljevich, B.; Dzubak, A. L.; Poloni, R.; Schnell, S. K.; Planas, N.; Kyuho, L.; Pascal, T.; Prendergast, D.; Neaton, J. B.; Smit, B.; Kortright, J. B.; Gagliardi, L.; Bordiga, S.; Reimer, J. A.; Long, J. R. *Nature* **2015**, *519*, 303.
4. Herm, Z. R.; Swisher, J. A.; Smit, B.; Krishna, R.; Long, J. R. *J. Am. Chem. Soc.* **2011**, *133*, 5664.
5. Bloch, E. D.; Murray, L. J.; Queen, W. L.; Maximoff, S. N.; Chavan, S.; Bigi, J. P.; Krishna, R.; Peterson, V. K.; Grandjean, F.; Long, G. J.; Smit, B.; Bordiga, S.; Brown, C. M.; Long, J. R. *J. Am. Chem. Soc.* **2011**, *133*, 14814.
6. Bloch, E. D.; Queen, W. L.; Krishna, R.; Zadrozny, J. M.; Brown, C. M.; Long, J. R. *Science* **2012**, *335*, 1606.
7. Herm, Z. R.; Wiers, B. M.; Mason, J. A.; van Baten, J. M.; Hudson, M. R.; Zajdel, P.; Brown, C. M.; Masciocchi, N.; Krishna, R.; Long, J. R. *Science* **2013**, *340*, 960.

Biography :

Jeffrey R. Long is a Professor of Chemistry and Chemical & Biomolecular Engineering at the University of California, Berkeley and a Senior Faculty Scientist in the Materials Sciences Division at Lawrence Berkeley National Laboratory. He served as Chair of the Division of Inorganic Chemistry of the American Chemical Society in 2012 and as a founding Associate Editor of the journal *Chemical Science*, and he is presently Director of the Center for Gas Separations. In 2014, he co-founded Mosaic Materials, Inc., a company devoted to the development of metal-organic frameworks for low-energy gas separations. His 260 publications have received more than 43,000 citations, and his recent awards include a UC Berkeley Graduate Assembly Faculty Mentor Award and the 2014 *Inorganic Chemistry* Lectureship Award.