

Light Gas Separations and Storage with MOFs *via* Modeling, Synthesis and Pressure Induced Structural Changes

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The ability to design, tune and test porous crystalline materials allows for the development of materials for many different environmental and energy applications. Metal-organic frameworks (MOFs) have shown great potential in challenging separations of molecules with very similar kinetic diameters. One area of strong focus in our lab is toward a fundamental understanding of the structure-property relationship of selective O₂ over N₂ adsorption in MOFs. Emphasis is placed on identifying key structural features for highly selective O₂ adsorption, leading to efficiency improvements in oxy-fuel combustion. Our approach involves predictive molecular modeling, experimental synthesis, and synchrotron crystallographic analysis of MOF materials. Density functional theory calculations were used to measure the binding energy for oxygen and nitrogen on coordinatively unsaturated metal sites in MOFs. Differential Pair Distribution Function analyses were used to determine guest-host structure relationships of both gas sorption and pressure induced gas retention in MOFs. Several different transition metal analogs of prototypical MOFs with these built-in features were evaluated. The effect of the metal on preferential guest binding was examined in detail. A post-synthetic metal substitution approach was considered for known isostructural series; this is useful in considering nontraditional metals in MOFs synthesis. Results indicate increased sensitivities in O₂/N₂ adsorption upon these modifications conducted at or near room temperature.

* Sandia National Laboratories is a multi-program lab managed and operated by Sandia Corp., wholly owned subsidiary of Lockheed Martin Corporation, for the US DOE's NNSA under contract DE-AC04-94AL85000. Work done at Argonne and use of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. DOE/Office of Science by Argonne National Laboratory, was supported by the USDOE, Contract No. DE-AC02-06CH11357.