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Efficient Light Gas Separations with MOFs *via* Predictive Modeling and Tuned Synthesis

Tina M. Nenoff, Dorina F. Sava Gallis, Marie V. Parkes, Jeffery A. Greathouse, Mark A. Rodriguez, Scott M. Paap, Christopher R. Shaddix
Sandia National Laboratories
Albuquerque, NM and Livermore, CA

The ability to design, tune and successfully test porous crystalline materials allows for the development and commercialization 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 O_2 over N_2 adsorption in MOFs. Emphasis is placed on identifying key structural features for highly selective oxygen adsorption, leading to efficiency improvements through oxy-fuel combustion.

Here we implement a synergistic approach involving predictive molecular modeling, experimental synthesis and guest-host crystallographic determination of known and novel MOF materials. Density functional theory (DFT) calculations were used to measure the binding energy for oxygen and nitrogen on coordinatively unsaturated metal sites 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. Guided by the modeling results, experiments were directed at both the synthesis of analogs of known materials and of novel frameworks. A post-synthetic metal substitution approach was considered for known insostructural series; this is useful in considering nontraditional metals in MOFs synthesis. Results indicate increased sensitivies in O_2/N_2 adsorption upon these modifications for single gas sorption measurements conducted at or in the room temperature range. Importantly, high oxygen selectivity over nitrogen is shown on a novel MOF material. Ongoing studies are evaluating the selectivities of the studied materials under industrially relevant mixed gas sorption studies. The focus is also placed on the modeling-directed design of novel MOFs with anticipated high performances.

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