347g Adsorption Fundamentals in Metal-Organic Frameworks from Molecular Modeling

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Metal-organic frameworks (MOFs) are a new class of nanoporous materials with potential applications in adsorption separations, catalysis, and gas storage. They also provide a unique opportunity to answer some fundamental questions about adsorption in nanoporous materials because it is possible to synthesize a series of MOF structures with the same framework topology but differing in their chemical constitution, pore size, and other factors. These highly tailorable materials are achieved via a self-assembly process using molecular building blocks. If nanoporous materials are to be truly designed, we must understand how the heat of adsorption, the surface area, and the free volume of the material affect adsorption and how the predetermined network governs these three key material properties. Molecular simulations, specifically grand canonical Monte Carlo (GCMC), allow for the investigation and comparison of adsorption in both existing and not-yet-synthesized MOF materials with a wide variety of internal structures. Our results of hydrogen and methane adsorption in various MOFs have allowed us to verify the existence of three regimes in gas adsorption. The first regime exists at low pressures where adsorption is primarily influenced by the heat of adsorption and the availability of low energy adsorption sites. When intermediate gas pressures are obtained, the available surface area of the material begins to dominate the comparative adsorption performance. Finally, at elevated pressures, the free volume of the material dictates the density of gas adsorbed within the material. There is an interplay among these important material properties that determines the relative ranking of a series of materials for adsorption of a particular adsorbate. Thus, proper engineering of the adsorbent requires knowledge of not only the desired gas to be adsorbed, but also the pressure range at which the material will be used.