Metal-Organic Frameworks for Highly Selective Separations

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This grant was focused on the study of metal-organic frameworks with these specific objectives. (1) To examine the use of MOFs with well-defined open metal sites for binding of gases and small organics. (2) To develop a strategy for producing MOFs that combine large pore size with high surface area for their use in gas adsorption and separation of polycyclic organic compounds. (3) To functionalize MOFs for the storage of inert gases such as methane. A brief outline of our progress towards these objectives is presented here as it forms part of the basis for the ideas to be developed under the present proposal.

This report does not contain any proprietary, confidential,
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A. Identification of Adsorption Sites in MOFs

Metal-organic frameworks (MOFs) have recently emerged as an important class of porous materials for their amenability to design and the flexibility with which their pores can be functionalized. In particular, their extraordinary low density (1.00 to 0.20 g/cm³) and high surface area (4500 m²/g) make them ideal candidates for the storage and separation of gases (N₂, Ar, CO₂, CH₄, and H₂). In this context, identifying the gas adsorption sites in MOFs is critically important to our ability to fine-tune those sites, sterically and electronically, in order to achieve the maximum storage capacity and selectivity. Traditionally, determination of adsorption sites in large-pore materials has been a challenge as the characterization techniques that are commonly applied to this problem, such as inelastic neutron scattering (INS) and diffuse reflectance infrared spectroscopy (DRIFTS), do not provide adequate information on the structural details of the

Fig. 1. (A) MOF-5 structure consists of a cubic array of Zn₄O(CO₂)₆ units connected by phenylene links (atoms shown as thermal ellipsoids of 90% probability, C: black, H: white, O: red, Zn: blue), which define large pseudo-cubic pores that can be completely evacuated. The yellow sphere represents the largest sphere that can occupy the pore without contacting the van der Waals surface of the framework. (B) A magnification of the corner of the pore schematically shows the location of adsorption site located equidistant to the three carboxylates. (C) The corresponding 3-D electron density map (F_{obs}) of this site, determined from single crystal X-ray diffraction data obtained at 293 K from crystals loaded under either N₂ or Ar. Only regions of electron density assigned to the framework atoms shown in (B) are observed. (D) At 30 K, regions of electron density assigned to adsorbed Ar or (E) N₂ become prominent. At 30 K, Fourier ripples around the Zn atoms can also be observed. Contours (e-/Å³): silver > 3, blue > 10, red > 60.

adsorption sites. A more precise technique is required to determine whether adsorption sites lie on the metal-oxide or the organic moieties, how many exist, and precisely where they are located in the MOF structure.

In this project, the primary adsorption sites for Ar and N₂ within metal-organic framework-5 (MOF-5), a cubic structure composed of Zn₄O(CO₂)₆ units and phenylene links defining large pores 12 and 15 Å in diameter, were identified by single crystal X-ray diffraction. Refinement of data collected

Fig. 2. At 30 K, eight symmetry-independent sites are crystallographically identified as partially occupied by argon atoms (shown as yellow spheres) in the pores of MOF-5. These include (A to C) three sites primarily associated with the secondary building unit and (D) those above the face and (E) edges of the linker.

between 293 and 30 K revealed a total of eight symmetry-independent adsorption sites. Five of these are sites on the zinc oxide unit and the organic link; the remaining three sites form a second layer in the pores (Fig. 1 and 2). The structural integrity and high symmetry of the framework is retained throughout, with negligible changes resulting from gas adsorption. We were able to identify the metrics and geometry of all the primary adsorption sites on the $\text{Zn}_4\text{O}(\text{CO}_2)_6$ and the C_6H_4 units of MOF-5, and uncover edge-wise $\text{C}_6\text{H}_4 \cdots \text{Ar}$ and $\text{C}_6\text{H}_4 \cdots \text{N}_2$ interactions previously unknown in gas-phase studies of aromatic van der Waals complexes.

B. Successful Deposition of Metal-Organic Polyhedra on Surfaces

Nano-sized metal–organic polyhedra (MOPs) are conveniently achieved by linking transition metal ions with either nitrogen or carboxylate donor organic units. We have shown the permanent porosity of MOPs by measurement of their gas adsorption isotherms; an important step toward their ultimate utility in separations. Further progress in this area hinged on our ability to functionalize the surface of such particles and to assemble them on substrates. Under this grant, the synthesis and X-ray single crystal structure of a MOP (termed MOP-18) of 5 nm in diameter was determined (Fig. 3). MOP-18 was dissolved in organic solvents and successfully deposited on a graphite substrate.

Studies focused on using these thin films for separation of organics and gas streams are already in progress. Films prepared from other MOPs (MOP-1) show high selectivity to carbon dioxide over methane, and preferential uptake of sulfur dioxide from air streams.

Fig. 3. (a) $\text{Cu}_2(\text{CO}_2)_4$ paddle-wheel unit and dodecoyl organic link (5- $\text{OC}_{12}\text{H}_{25}$ -*m*BDC), (b) a rhombicuboctahedral framework of 13.8 Å diameter void (yellow), and (c) crystal structure of MOP-18 (Cu, blue; O, red; C, black).

Fig. 4. STM image of MOP-18 on graphite substrate (25 °C, ambient pressure): (a) large-scale image showing the long range ordering, and (b) enlarged image with an overlaying hexagon having a side 3.7 nm.

C. Porous Metal-Organic Frameworks Constructed from Rod Building Units

The principal structure possibilities for packing metal-carboxylate infinite rod-shaped building blocks were determined (Fig. 5). Some basic nets derived from linking simple rods (helices and ladders) were then enumerated.

We demonstrated the usefulness of the concept of rod building units in the design and synthesis of MOFs by preparing, characterizing and studying the adsorption chemistry of 14 new MOFs (named MOF-69A to C and MOF-70 to 80) belonging to 12 different structure types of rod packing motifs. It was possible to show how their structures are related to these basic nets enumerated earlier. These MOFs are of polytopic carboxylates and contain one of Zn, Pb, Co, Cd, Mn, or Tb. The inclusion properties of the most open members were presented as evidence that MOF structures with rod building blocks can indeed be designed to be useful in adsorption of gases and organics.

A specific example of MOFs based on rod building units is MOF-74 (Fig. 6). This structure has one dimensional channel with high porosity ($2,000 \text{ m}^2/\text{g}$). Using powder samples of MOF-74, it is possible to selectively remove carbon monoxide from mixtures of methane and carbon dioxide. This material is already being scaled up by BASF (Ludwigshafen, Germany) at the cubic meters level for use in gas separations and polymerization reactions to make polypropylene carbonates. At present, other MOFs based on rod building blocks are proving to be useful in providing highly polarizable sites for hydrogen storage due to the high density of metal oxide units in their backbone structure.

Fig. 5. Topologies of the most likely structures to result from assembly of rod shaped building units. Rods colored in red, green, yellow and blue are metal oxides linked by organic units (gray). In 1-4, the rods are pointing into the page.

Fig. 6. The structure of MOF-74: The zinc oxide rod building units are shown in as polyhedral running into the page and linked together via benzene ring of 2,5-dihydroxy-1,4-dicarboxylate.

D. Publications Resulting from this Funding Period

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