IV.D.3 Hydrogen Storage in MOFs

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Objectives

- Utilize new concepts for increased surface area.
- Implement strategies for higher adsorption energy.
- Develop strategies for increased hydrogen density in metal-organic framework (MOFs).

Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

- Volumetric density: 45 g/L
- Gravimetric density: 60 mg/g

Accomplishments

- Collected hydrogen adsorption data for seven MOF materials at 77 K which leads to saturation at pressures between 25 and 80 bar.
- Reported uptake from 2.0 wt% to 7.5 wt% at 77 K.
- Showed that hydrogen saturation uptake in MOFs correlates well with surface area and, contrary to

a widely held belief, viable volumetric densities in highly porous structures can indeed be achieved.

Introduction

Conventional storage of large amounts of hydrogen in its molecular form is difficult and expensive because it requires employing either extremely high pressures as a gas or very low temperatures as a liquid. The desire to store hydrogen with sufficient efficiency to allow its use in stationary and mobile fueling applications is spurring a worldwide effort in new materials development. The Department of Energy, in its 2010 guidelines, has set performance targets for on-board automobile storage systems to have densities of 60 mg H_2/g (gravimetric) and 45 g H_2/L (volumetric). Given that these are system goals, a practical material will need to have higher capacity when the weight of the tank and associated cooling or regeneration system is considered. The size and weight of these components will vary substantially depending on whether the material operates by a chemisorption or physisorption mechanism. In the latter, case metal-organic frameworks (MOFs) have recently been identified as promising adsorbents for H_2 storage, although little data are available for their sorption behavior at saturation, a critical parameter for gauging the practicality of any material.

Approach

Metal-oxide secondary building units (SBUs) and the organic carboxylate links of the MOFs were investigated here. The isoreticular MOF (IRMOF) series, IRMOF-1, -6, -11, and -20, is derived from linking the basic zinc acetate unit, $Zn_4O(CO_2)_6$, with linear ditopic carboxylates. MOF-177 is constructed from this same SBU and the tritopic link benzenetribenzoate. MOF-74 is constructed from infinite 31 (or 32) helical rods of composition $Zn_3[(O)_3(CO_2)_3]$ and HKUST-1 is composed of the $Cu_2(CO_2)_4$ paddle-wheel SBU linked by benzene-1,3,5-tricarboxylate.

The MOFs chosen represent a subset of well characterized materials that exhibit some of the highest surface areas experimentally determined to date (Figure 1). These materials vary in chemical functionality, metrics of the link, and the nature of the SBU. Their structures are derived from non-interpenetrated nets, with the exception of the doubly interpenetrated IRMOF-11, and three distinct SBUs. Crystalline samples of all the MOFs were prepared and activated prior to sorption measurements according to recently optimized procedures.
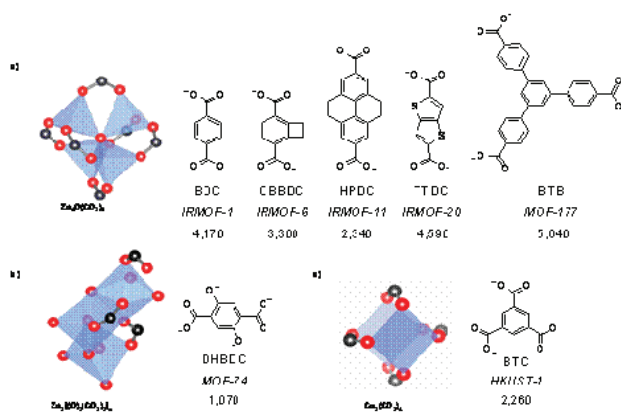
FIGURE 1. MOF Structures

FIGURE 2. Gravimetric Density of Hydrogen Uptake in MOFs at 77K

Results

Figure 2 shows the resulting H_2 sorption isotherms up to 90 bar at 77 K where saturation binding of H_2 is achieved. The isotherms do not show significant hysteresis, consistent with physisorption of supercritical H_2. The saturation uptakes vary widely: for MOF-74 the uptake at saturation (26 bar) is 2.3 wt% and 3.5 wt% for IRMOF-11 (34 bar), whereas for MOF-177 and IRMOF-20 saturation is reached between approximately 70 and 80 bar, giving H_2 uptakes of 7.5 wt% and 6.7 wt%, respectively. A plot of gravimetric uptake as a function of apparent surface area reveals a nearly linear correspondence (Figure 3). This result stands in stark contrast to those obtained at low pressures where MOF-74, HKUST-1 and IRMOF-11, the three lowest surface area materials, showed maximal uptake. This difference may arise from binding to relatively higher affinity open-metal sites (present in MOF-74 and HKUST-1) or to constricted pores in IRMOF-11. Although gravimetric capacity is often a major target for research in H_2 storage materials, there are practical limits associated with the tank volume required to house the sorbent which makes volumetric capacity just as critical a parameter to consider. Accordingly, the gravimetric data have been converted to volumetric units (g H_2/L) using the crystallographic densities of each MOF (Figure 4). By this metric, the MOF materials are much more similar in their sorption capacities due to canceling effects derived from the different densities of the materials. It should be noted that bulk packing densities will vary somewhat between materials and decrease the practical volumetric capacity in a storage system. IRMOF-20 and MOF-177 show the best uptake on a volumetric basis due to a combination of substantial H_2 uptake and moderate densities. The values of 34 g/L for IRMOF-20 and 32 g/L for MOF-177 are well within the realm of the 2010 DOE target of 45 g/L.
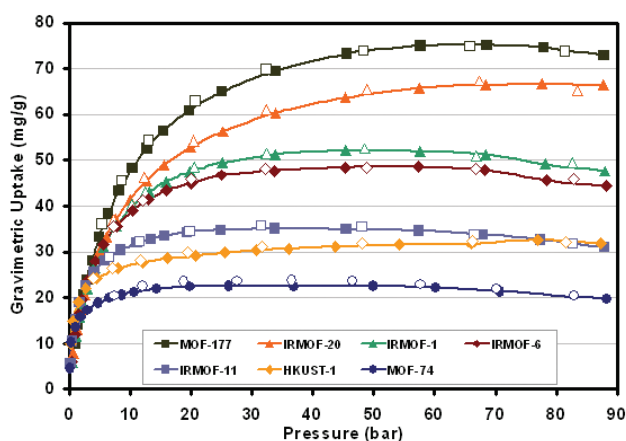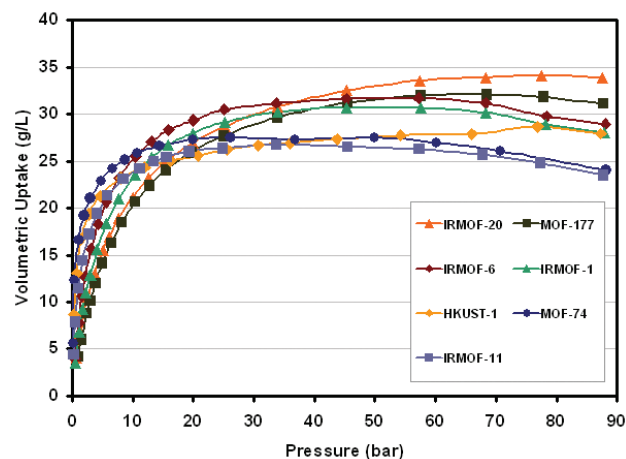

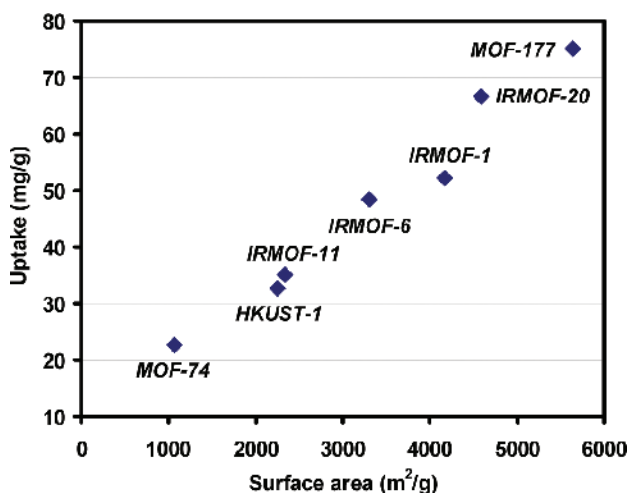**FIGURE 3.** Volumetric Density of Hydrogen Uptake at 77K

FIGURE 4. Correlation of Uptake with Surface Area

Conclusions and Future Directions

Demonstrates that the volumetric capacity of MOFs is feasible as a storage medium and dispels the misconception that porous materials will inherently have poor volumetric storage capacity.

Highly porous materials can have small pores. MOF-74 has the highest density of any of the MOFs examined here ($1.22 g/cm^3$ compared to $0.477 g/cm^3$ for MOF-177 which is the lowest) and thus shows a volumetric uptake of 28 g/L which is better performance than the gravimetric results taken alone imply. Although the density of IRMOF-11 is approximately 50% greater that MOF-177 it is still the lowest performing material on a volumetric basis.

In future, we will design means of increasing the uptake at room temperature.

FY 2006 Publications/Presentations

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2. Determination of the hydrogen absorption sites in $Zn_4O(1,4-benzenedicarboxylate)_3$ by single crystal neutron diffraction, E. Spencer, J. A. K. Howard, G. McIntyre, J. Roswell, O. M. Yaghi, *Chem. Comm.*, **2006**, 278-280.

3. Effects of functionalization, catenation, and variation of the metal oxide and organic linking units on the low-pressure hydrogen adsorption properties of metal-organic frameworks, J. L. C. Roswell, O. M. Yaghi, *J. Am. Chem. Soc.*, **2006**, *128*, 1304-1315.

4. Characterization of H-2 binding sites in prototypical metal-organic frameworks by inelastic neutron scattering, J. L. C. Roswell, J. Eckert, O. M. Yaghi, *J. Am. Chem. Soc.*, **2005**, *127*, 14904-14910.

5. Design, synthesis, structure, and gas (N_2, Ar, CO_2, CH_4 and H_2) sorption properties of porous metal-organic tetrahedral and heterocuboidal polyhedra, A. Sudik, N. Ockwig, A. Millward, A. P. Côté, O. M. Yaghi, *J. Am. Chem. Soc.*, **2005**, *127*, 7110.

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7. Strategies for hydrogen storage in metal-organic frameworks, J. Roswell, O. M. Yaghi, *Angew. Chem. Int. Ed.,* **2005**, *44*, 4670.