

IV.D.3 Hydrogen Storage in Metal-Organic Frameworks

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- Volumetric density: 45 g L⁻¹
- Gravimetric density: 60 mg g⁻¹

Accomplishments

- Collected H₂ adsorption data for a series of MOF materials at 77 K. The results indicate that open metal sites and catenation of frameworks improve interaction between H₂ and adsorbents.
- Impregnation of MOF-177 with polymer precursor and successive polymerization reaction.
- Considered relationship between ΔH values and pore structures.
- Began metal-doping experiments and post-synthesis reaction for immobilization of metal complexes.
- Demonstrated the stability and durability of MOF-177. The measurement confirms that at least 4 wt% of H₂ would be delivered under the present experimental condition (2-60 bar and 77 K).



Objectives

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

- (A) System Weight and Volume
- (C) Efficiency
- (E) Charging/Discharging Rates
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

This project consists of conducting fundamental studies of MOFs. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2010 hydrogen storage targets:

Introduction

Conventional storage of large amounts of hydrogen in its molecular form is difficult and expensive because it requires employing either extremely high pressure as a gas or very low temperature as a liquid. Because of the importance of hydrogen as a fuel, the DOE has set system targets for H₂ storage; the gravimetric (6.0 wt%) and volumetric (45 g L⁻¹) densities to be achieved by 2010. MOFs exhibit the highest hydrogen uptake of any porous materials and clearly show that in principle the DOE targets can be achieved at 77 K. The implementation of room temperature hydrogen storage in MOF materials will require the design of new porous solids. We are therefore undertaking efforts to discover highly porous materials with strong affinity for hydrogen.

Approach

To meet the DOE 2010 targets by physisorption, adsorbents must have high surface area (>3,500 m² g⁻¹) and relatively high density (>0.75 g cm⁻³). We have already demonstrated how to design high surface area materials; however, in many cases these materials do not show steep H₂ uptakes in the low pressure region, which is indicative of the weak interaction with H₂. This behavior is in sharp contrast to zeolites and activated carbons as well as smaller pore MOFs. Therefore, (in the middle of this year) we investigated the relationship between adsorption enthalpy (ΔH) and initial slope (Henry's constant, K_H) for many porous materials. Our

studies indicate that ΔH is generally proportional to K_H . However, some smaller pore materials show a smaller ΔH value than expected from the K_H value. In other words, smaller pore materials may confine H_2 at 77 K because the effect of entropy is not as large. Nevertheless, storage capacity decreases drastically with an increase in storage temperature; therefore smaller pores are not an effective strategy for the room temperature H_2 storage. Our analysis suggests that greater adsorption enthalpy is the key issue for the improvement of H_2 uptake at room temperature. To that end, we must design MOFs that contain both strong binding sites and high surface areas. In this fiscal year, we implemented the strategy to improve the adsorption enthalpy in MOF systems.

Results

To improve the adsorption enthalpy of MOFs the following strategies were examined: (i) combination of interpenetration with open metal sites, (ii) introduction of links containing B and N as strong polarizing atoms, and (iii) impregnation of MOFs with polymers and metals. Figure 1 demonstrates metal-oxide secondary building units (SBUs) and the organic carboxylate links of the MOFs we tested. MOF-324 whose connectivity is a simple cubic system is constructed from a Zn cluster and ditopic link. The MOF-326 and 177 are derived from a basic zinc acetate unit, $Zn_4O(CO_2)_6$, with ditopic and tritopic carboxylates, respectively. Interpenetrated structures of MOF-14 and 601 are composed of the

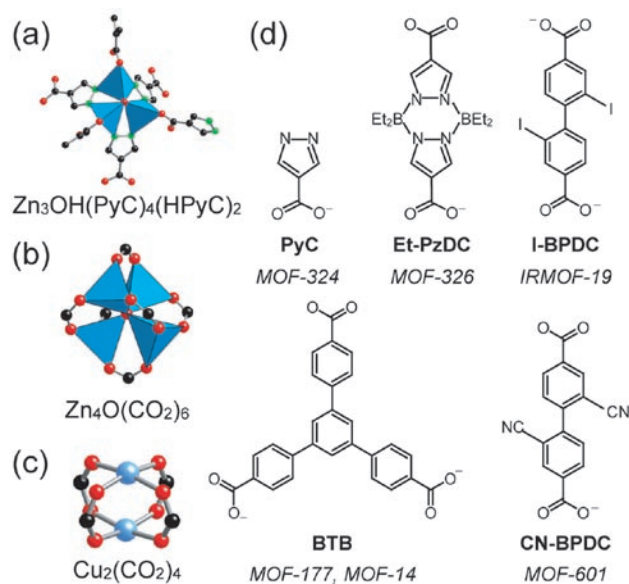


FIGURE 1. (a) SBU of MOF-324 is comprised of a Zn_3OH cluster, two PyC and one HPyC group. (b) $Zn_4O(CO_2)_6$ -based MOFs in italics derived from the link in parentheses: MOF-326 (Et-PzDC), IRMOF-19 (I-BPDC), and MOF-177 (BTB). (c) MOF-14 and -601, $Cu_2(CO_2)_4$ -based MOFs with BTB and CN-BPDC, respectively.

$Cu_2(CO_2)_4$ paddle-wheel SBU linked by tritopic and ditopic carboxylates.

Combination of Interpenetration with Open Metal Sites: It is known that interpenetration of the framework as well as open metal sites improve H_2 uptake in the low-pressure region. Therefore, low-pressure H_2 isotherms for two interpenetrated MOFs (MOF-14 and 601) having Cu paddle-wheel units were tested (Figure 2). MOF-14 adsorbs a significant amount of H_2 (19 mg g^{-1}) at 77 K and 1 bar. This is higher than that for MOF-177 under the same condition [1]. On the other hand, MOF-601 does not show high H_2 uptake (9 mg g^{-1}). Considering that MOF-601 has the large 1D open channel (*ca.* 1.5 nm), it can be concluded that improvement of H_2 uptake in the low-pressure region is expected when the smaller pore diameter is achieved by interpenetration of the frameworks.

Although H_2 uptake in MOF-601 at 1 bar is not great, the inner surface of MOF-601 is decorated with cyano (CN) groups. To evaluate the effect of CN groups on H_2 uptake, the coverage dependencies of ΔH for H_2 were calculated from fits of their 77 and 87 K isotherms. As shown in Figure 3, initial value of ΔH for MOF-601 is even higher than that for MOF-14 which also has open metal sites (7.7 kJ mol^{-1} for MOF-601, 7.0 kJ mol^{-1} for MOF-14). The finding implies that CN groups in the pore can improve adsorbent- H_2 interaction. On the other hand, ΔH value for MOF-14 is almost constant. This may be because the 1,3,5-benzenetribenzoate (BTB) link has weaker interaction with H_2 compared to CN-BPDC.

Introduction of Links Containing B and N: MOF-326 and MOF-5, which feature the same connectivity, differ only in the organic link. We selected this link

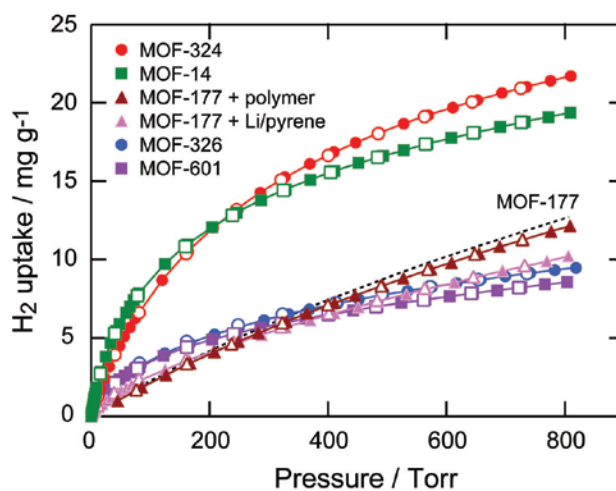


FIGURE 2. H_2 adsorption isotherms for MOFs measured at 77 K in gravimetric units. Data for MOF-177 is shown for comparison. Adsorption data are shown as closed circles, desorption data as open circles, and connecting traces are guides for the eye.

due to the fact that the boron and nitrogen atoms in the link are negatively and positively charged, respectively, which may improve H₂-MOF interaction. The shape of the isotherm and H₂ uptake at 1 bar is close to those of MOF-601 (Figure 2). Surprisingly, small hysteresis was observed despite the fact that hysteresis is not expected under supercritical H₂ adsorption measurement. Currently we do not know the reason, but we can point out several possibilities: this small hysteresis can be attributed to (i) structural distortion during the adsorption measurement and (ii) strong interaction between H₂ and organic link. The ΔH at zero coverage for MOF-326 is estimated to be 7.1 kJ mol⁻¹ and shows gradual decrement to 4.5 at 7 mg g⁻¹ of surface coverage (Figure 3). The initial value is higher than those of Cu₃(benzene-1,3,5-tricarboxylate)₂ (HKUST-1) and MOF-505 (MOFs with open metal sites, 6.5-7.0 kJ mol⁻¹), even though MOF-326 does not have either open metal sites or interpenetrating frameworks. This indicates that polarized B-N bonds improve the H₂ binding energy.

When 2,8-pyrazabole dicarboxylic acid (H₂PzDC) is used as a starting material, MOF-324 is obtained, although MOF-324 does not contain 2,8-pyrazabole dicarboxylate (PzDC) linkers. Instead, the 4-pyrazole carboxylate (PyC) link is formed from PzDC through in situ ligand generation. MOF-324, also having similar cubic framework to MOF-5, shows good performance for H₂ adsorption (21 mg g⁻¹). Considering that MOF-324 does not have open metal sites, it is probable that the effective H₂ uptake is attributed to the small pore diameter (7.6 Å), which is roughly three times larger than the kinetic diameter of dihydrogen. Furthermore, two nitrogen atoms in PyC link increase the polarization of the adsorbent, leading to improvement of adsorption enthalpy. The estimated adsorption enthalpy for MOF-324 (6.2 kJ mol⁻¹) was higher than that for MOF-177 but slightly lower than HKUST-1. While the relatively high binding energy in HKUST-1 originates mainly

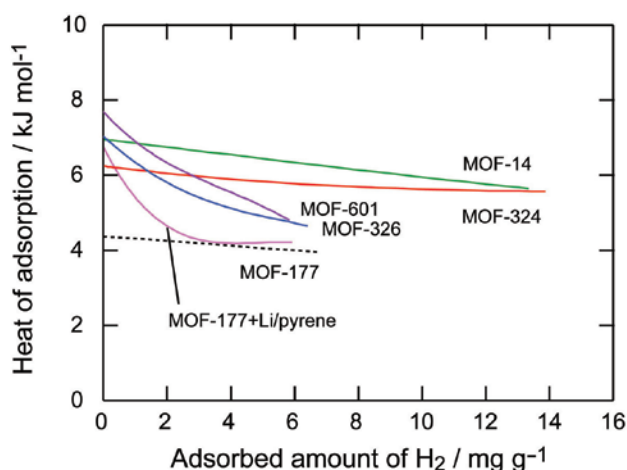


FIGURE 3. Coverage dependencies of the isosteric heats of adsorption for H₂ in MOFs calculated from fits of their 77 and 87 K isotherms.

from the presence of open metal sites, this cannot be the case for MOF-324. We attribute this effect to in MOF-324 the small pore diameter, which facilitates stronger binding of H₂ by interactions with many more surface sites. This idea is supported by inelastic neutron scattering experiments; the data suggest the presence of interatomic interactions of H₂ due to the much reduced pore size.

Impregnation of MOFs with Polymers: Since interpenetration of the framework improves adsorbent-H₂ interaction, it is reasonable to consider that impregnation of MOFs with polymers can work to confine light gas molecules. However, it is not realistic to impregnate polymers directly because of their bulkiness and slow diffusion rate. Therefore, polymer precursors (1,4-diphenylbutadiyne) were impregnated and were polymerized successively. The low-pressure H₂ uptakes at 77 K are almost inversely proportional to the amount of polymer in the pore, and no samples showed significant improvement of binding energy.

High-Pressure H₂ Isotherms: Figure 4 shows the H₂ adsorption isotherms up to 80 bar at 77 K. These isotherms do not show significant hysteresis, consistent with physisorption of supercritical H₂. The excess H₂ uptake values vary widely; for MOF-324, the uptake at saturation (33 bar) is 33 mg g⁻¹ and 39 mg g⁻¹ for MOF-14 (46 bar), whereas for MOF-601, saturation is not reached under present experimental condition, giving maximum H₂ uptakes of 34 mg g⁻¹. A plot of gravimetric uptake as a function of apparent surface area reveals a nearly linear correspondence [2]. It is interesting to note that H₂ uptake for these materials is slightly greater than other MOFs reported previously. The finding

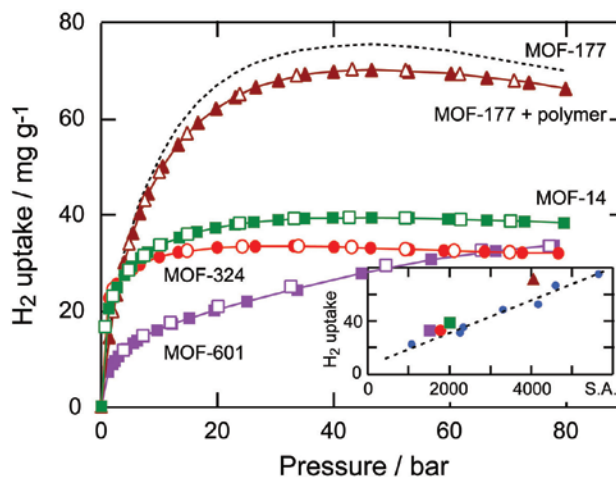


FIGURE 4. High-Pressure H₂ Isotherms for MOFs at 77 K: as a reference, isotherm for MOF-177 is shown as broken curve. Filled and open symbols represent adsorption and desorption branches, respectively. Connecting traces are guides for eyes. Inset: H₂ uptake plotted against Langmuir surface area. Regression line for blue circles (from [2]) is also overlaid.

demonstrates that control of pore size distribution and addition of open metal sites leads to moderate improvement at 77 K, but not enough to meet the DOE targets.

The gravimetric data have been converted to volumetric units (g L^{-1}) using the density of each MOF. Again, these values increase with an increase in the surface areas (total free volume). This trend is more remarkable when the absolute H_2 uptakes (not excess H_2 uptakes) are plotted to the surface areas. However, the contribution from bulk H_2 should be 30-40% at 77 K and 70 bar. Considering that the bulk density at room temperature is roughly one fourth compared to 77 K, there will be far fewer H_2 molecules in a given MOF if ΔH is not improved. Indeed, our high-pressure H_2 isotherms at room temperature support the importance of higher binding energy; volumetric H_2 uptakes (total H_2 uptakes) at 298 K in MOFs are slightly higher than the density of bulk H_2 at same temperature and pressure.

Design and Synthesis of Metal-Doped MOFs: We originally attempted impregnation of MOF-177 with ferrocene (Fc) to introduce high affinity sites for H_2 storage. Since the metal atom of Fc is not exposed, H_2 uptake amount in the low-pressure region was not improved. Thus, the immobilization of high affinity sites within the pore structure of MOFs still needs to be addressed. Therefore, we performed post-synthetic modification using Fc derivatives as a proof of principle. IRMOF-3, which is amino-functionalized MOF-5, was reacted with ferrocene aldehyde to form a covalent bond; $\text{MOF-NH}_2 + \text{Fc-CHO} \rightarrow \text{MOF-N=CH-Fc}$. After reaction, modified material was black in color, indicating that Fc molecules were immobilized through covalent bonds. Unfortunately, H_2 uptake capacity for Fc-IRMOF-3 material was lower than pristine IRMOF-3, although initial ΔH value was slightly improved. However, this immobilization method can be applicable to other molecules possessing a formyl group. For example, if IRMOF-3 is reacted with 2-hydroxybenzaldehyde, the resultant may form metal complexes with various metals (e.g. Cu, Zn, Ni, Co).

A second approach is lithium impregnation [3]. Originally, we attempted impregnation of MOFs with lithium metal by liquid phase adsorption; however impregnated MOFs showed poor porosity. Therefore, impregnation with a lithium hydrocarbon complex, used commonly as lithium transfer reagents, was performed. If the hydrocarbon can be removed from the pores by thermal treatment (decomposition of Li-hydrocarbon complex) and successive washing with organic solvents (removal of hydrocarbon), lithium can be immobilized in the MOFs.

After impregnation of Li-pyrene, the surface area and pore volume of the impregnated material were almost half that of the pure MOF-177 ($2,920 \text{ m}^2 \text{ g}^{-1}$, $1.03 \text{ cm}^3 \text{ g}^{-1}$). The decrease in surface area is attributed

to the remaining pyrene molecules even after thermal treatment. We also used Li-naphthalene; however the naphthalene molecules could not be removed. Due to the remaining pyrene, H_2 uptake of the impregnated material at 1 bar is not high, though the initial slope of the isotherm is greater than pristine MOF-177. Indeed, the estimated ΔH value for the Li-pyrene impregnated MOF-177 is improved by 50% over MOF-177 (Figure 3). Although current H_2 uptake is not enough to meet the DOE target, we believe that impregnation of metal is a promising way to realize the high affinity sites.

Finally, to investigate the possibility of introducing a carbon-lithium bond into a MOF after synthesis of the framework, a novel MOF bearing iodo-groups was synthesized (Figure 1). IRMOF-19 is a doubly interpenetrated MOF-5 type structure with two iodo groups on each link. According to theoretical calculations, it is possible to store 4-5 wt% of H_2 if each iodo-group is replaced with lithium and if three H_2 molecules are coordinated to each lithium atom. After the halogen-lithium exchange reaction, we tested the H_2 adsorption. However, H_2 isotherms for the sample after the reaction do not show any difference, indicating that an exchange reaction didn't occur under the present conditions. We will modify reaction conditions to accelerate the reaction rate for halogen-lithium exchange.

Toward the Practical use of MOFs: The effect of H_2 impurities on the reversibility, kinetics, and durability were tested. MOF-177 is not damaged as long as the purity of H_2 is high, while the H_2 uptake (measured gravimetrically) was increased when we used low-quality H_2 . Although there is no direct evidence, the increase in the uptake can be attributed to the adsorption of impurities (e.g. water). However, no significant change in kinetics is observed in both experiments. After a cycling test using low-purity H_2 we recorded a high-purity H_2 isotherm. Considering that the H_2 uptake was somewhat lower than that for fresh material (i.e. $75 \text{ mg/g} \rightarrow 71 \text{ mg/g}$), water molecules in the H_2 cylinder may have a negative impact on the sample quality. However, we believe the impurities in the cylinder should not be a critical problem for reversibility or durability because most condensable impurities should be removed easily by passing through an adsorbent bed. We expect that liquid N_2 traps for gas purification would be supplied in each H_2 station.

Conclusions and Future Directions

For cryogenic H_2 storage, the combination of interpenetration and open metal sites can improve gravimetric H_2 uptake capacity, which is evidenced by the correlation between surface area and H_2 uptake. However, volumetric uptake for these MOFs at room temperature is still close to the bulk H_2 density under same conditions. This result indicates that effective

MOFs must be replete with strong binding sites, even though the surface area (or pore volume) of such MOFs could be compromised. In the future we will put to use insights gained by theoretical prediction to design MOFs with high uptake at room temperature:

- Employ light weight metals to create strong binding sites.
- Implement the concept of “soft chemisorption”.
- Material design based on theoretical prediction.

Special Recognitions & Awards/Patents Issued

1. 15th most highly cited chemists; over 100 citations per paper (1997-2007).
2. Materials Research Society, MRS Medal Recipient.
3. Dean’s Recognition Award, UCLA.

FY 2008 Publications/Presentations

1. *Independent Verification of the Saturation Hydrogen Uptake in MOF-177 and Establishment of a Benchmark for Hydrogen Adsorption in Metal-Organic Frameworks*, H. Furukawa, M.A. Miller, and O.M. Yaghi, *J. Mater. Chem.*, **2007**, *17*, 3197.
2. *Impact of Preparation and Handling on the Hydrogen Storage Properties of $Zn_4O(1,4\text{-benzenedicarboxylate})_3$ (MOF-5)*, S. Kaye, A. Dailly, O.M. Yaghi, and J. Long, *J. Am. Chem. Soc.*, **2007**, *129*, 14176.

3. *Control of Vertex Geometry, Structure Dimensionality, Functionality and Pore-Metrics in the Reticular Synthesis of Crystalline Metal-Organic Frameworks and Polyhedra*, H. Furukawa, J. Kim, N.W. Ockwig, M.O’Keeffe, and O.M. Yaghi, *J. Am. Chem. Soc.*, **2008**, *130*, 11650.
4. *Tuning Pore Sizes in Metal-Organic Frameworks: Interpenetration and in situ linker formation*, D.J. Tranchemontagne, K.S. Park, H. Furukawa, J. Eckert, C. Knobler, and O.M. Yaghi, *J. Am. Chem. Soc.* in preparation.

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3. S.S. Han and W.A. Goddard, *J. Am. Chem. Soc.*, **2007**, *129*, 8422.