

IV.C.9 Hydrogen Storage in Metal-Organic Frameworks

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Fiscal Year (FY) 2011 Objectives

- Expand the framework while keeping strong H₂ binding sites:
 - Design new porphyrin metal-organic frameworks (MOFs) to increase the storage space.
 - Expand Mg-MOF-74; high Q_{st} and Brunauer-Emmett-Teller (BET) surface area to achieve high H₂ density at room temperature.
- Preparation of high-surface area MOFs:
 - Large storage space, with minimization of dead space (*i.e.* high BET surface area).
 - Evaluate room temperature H₂ storage capacity by new high surface area MOFs.

Technical Barriers

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

- (A) System Weight and Volume
- (C) Efficiency
- (E) Charging/Discharging Rates

Technical Targets

This project consists of conducting fundamental studies of MOFs. Insights gained from these investigations will be applied toward the design and synthesis of hydrogen

storage materials that meet the following DOE 2015 revised hydrogen storage targets:

- Volumetric density: 40 g L⁻¹
- Gravimetric density: 4.5 wt%

FY 2011 Accomplishments

- Preparation of novel MOFs with metals.
- Highest BET surface area among porous solids.
- Fifteen and 2.7 wt% H₂ uptake by MOF-210 at 77 and 298 K.



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. Due to the described importance of hydrogen as a fuel, the DOE has set system targets for H₂ storage for the gravimetric (5.5 wt%) and volumetric (40 g L⁻¹) densities to be achieved by 2015. MOFs exhibit the highest hydrogen uptake of any porous materials and clearly demonstrate that the DOE targets are possible to achieve at 77 K. However, the implementation of room temperature hydrogen storage in MOF materials will require the design of new porous solids. Therefore, we are currently focusing our efforts on discovering novel highly porous materials with strong affinity for hydrogen.

Approach

To meet the DOE 2015 revised targets via 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 most cases these materials do not demonstrate steep H₂ uptake in the low pressure region, which is indicative of the weak interaction with H₂. Therefore, we aimed at increasing strong binding sites for maximum H₂ uptake capacity without losing pore volume. More specifically, we prepared and tested the H₂ storage capacity of three types MOFs: (i) metalated MOFs, (ii) MOFs with open metal sites and large pore, and (iii) ultrahigh surface area MOFs, which are materials having the highest BET surface area.

Results

Preparation of Porphyrin MOFs. To achieve strong H₂-MOF interaction, we believe that utilization of open metal sites is essential and the most effective method.

Several metal ions are known to form coordinatively unsaturated sites; however, it is fair to say that only a limited number of metal units, e.g. $\text{Cu}_2(\text{CO}_2)_4$ are available in MOF structure. In other words, it is important to design novel MOFs whose organic linker has potential metal binding site. We have prepared MOFs with porphyrin linkers that are connected by zinc paddle wheel units. However, H_2 uptake in these porphyrin MOFs is not high, likely due to moderate surface areas. To overcome this drawback, we prepared a new MOF with Zr ions.

Based on the reticular chemistry of these systems, it is expected that the $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{CO}_2)_{12}$ units (Figure 1A) are connected by tetratopic links to form new MOF structures, i.e. **ftw** net for square tetratopic link, **ith** net for tetrahedron. Therefore, we chose tetraphenylporphyrin as a square tetratopic link (Figure 1A) to synthesize a new free-base porphyrin MOF and its metalated versions (Cu and Pd ions). The porphyrin MOFs were prepared by a solvothermal reaction of a mixture of porphyrin link and zirconium chloride in *N,N*-dimethylformamide. Although, we did not finalize the structure, the powder X-ray diffraction pattern of this material is nearly identical to the simulated pattern of modeled material.

The permanent porosity was demonstrated by Ar adsorption isotherm for guest free samples. The compound shows typical type I isotherm, which indicates that the material has microporosity. The BET surface areas of

activated MOFs are estimated to be 2,100, 1,850, and 1,700 m^2/g for free-base, Cu and Pd porphyrin MOFs, respectively. To evaluate the pore size distribution of porphyrin MOF, the Ar isotherm was analyzed using nonlocal density functional theory. The distribution calculated by fitting the adsorption data (17 Å) is close to the pore diameter from modeled structure of each MOF.

The H_2 isotherms of porphyrin MOFs were measured at 77 and 87 K. The H_2 uptake of free-base, Cu and Pd porphyrin MOFs at 1 bar and 77 K is 1.6, 1.7, and 1.6 wt%, respectively. These uptakes are larger than that of MOF-177. We also estimated the heat of adsorption (Q_{st}) and the initial Q_{st} value of the free-base porphyrin MOF was calculated to be 6.4 kJ/mol, which is similar to MOF-199 having open metal sites (6.8 kJ/mol) [1]. More importantly, the initial Q_{st} values of metalated porphyrin MOFs (7.0 and 6.8 kJ/mol for Cu and Pd version) were higher than that of free-base porphyrin MOF, indicating that the metal ions in the large aromatic (porphyrin) cycle can improve the H_2 -MOF interaction. For the room temperature H_2 storage, further improvement of the Q_{st} is required; therefore, we plan to synthesize other metalloporphyrin MOFs.

Preparation of Expanded Version of Mg-MOF-74.

To achieve room temperature H_2 adsorption, density of strong H_2 binding site per volume is one of the key factors. We have demonstrated that rod-type metal building units (Figure 1B) are sufficient systems for increasing the metal/

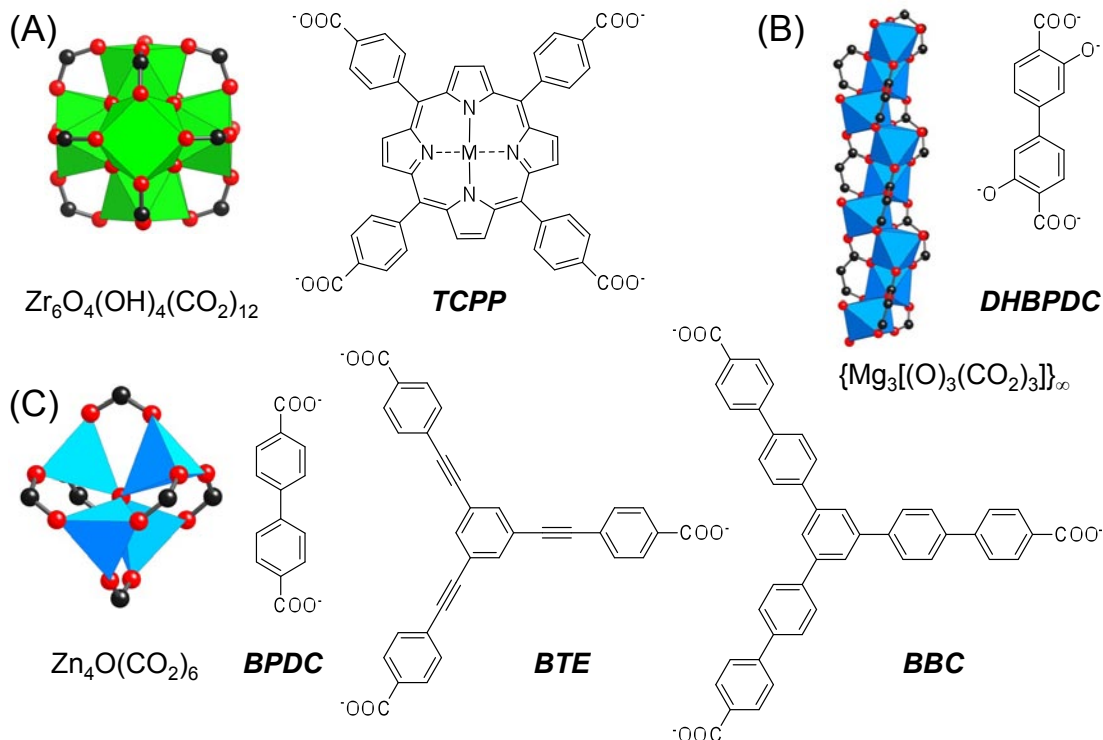


FIGURE 1. (A) $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{CO}_2)_{12}$ -based MOFs with porphyrin linkers (TCPP, $\text{M} = \text{H}_2$, Cu, or Pd). (B) Expanded version of Mg-MOF-74 is prepared using 3,3'-dihydroxy-[1,1'-biphenyl]-4,4'-dicarboxylate (DHPDC). (C) $\text{Zn}_4\text{O}(\text{CO}_2)_6$ unit is connected with organic linkers to form MOF-210 (BPDC and BTE) and MOF-200 (BBC).

ligand ratio (for example, MOF-74 shows excellent H_2 uptake behavior in the low pressure region at 77 K [1]). However, because of the moderate pore diameter of MOF-74, the surface area of MOF-74 is not high enough to meet the DOE targets of 5.5 wt%. We believe that expansion of the one-dimensional channel diameter would increase the total storage capacity. In this year, we prepared extended version of Mg-MOF-74 using 3,3'-dihydroxy-[1,1'-biphenyl]-4,4'-dicarboxylic acid (Figure 1B, this linker was provided by Prof. Stoddart group of Northwestern University) by a solvothermal reaction. Obtained micro crystals were analyzed by powder X-ray diffraction (PXRD) measurements.

To confirm the porosity and estimate the pore size distribution, we recorded Ar isotherm for the activated sample of expanded Mg-MOF-74 at 87 K. The compound shows a step at $P/P_0 = 0.05$, which indicates that the material has relatively large pore. The Langmuir and BET surface areas of activated MOF are estimated to be 3,200 and 2,740 $m^2 g^{-1}$, respectively. The pore size distribution calculated by fitting the Ar adsorption data (19 Å) is close to the pore diameter from the crystal structure.

To calculate the Q_{st} for this MOF, low-pressure H_2 isotherms were recorded at 77 and 87 K. The initial Q_{st} value (10.1 kJ/mol) is almost the same as that of Mg-MOF-74 (10.1 kJ/mol [2]). The Q_{st} curves are sometimes influenced by the pore geometry with smaller pore materials tending to show better Q_{st} data. However in this case, it seems the initial Q_{st} value just reflects the Mg- H_2 interaction.

Figure 2 demonstrates a high-pressure excess H_2 isotherm of expanded MOF-74 at 77 K (red circles). The isotherm showed a steep raise below 10 bar, the excess uptake was saturated around 45 bar where the H_2 uptake was 4.5 wt%. As expected, the profile of high-pressure

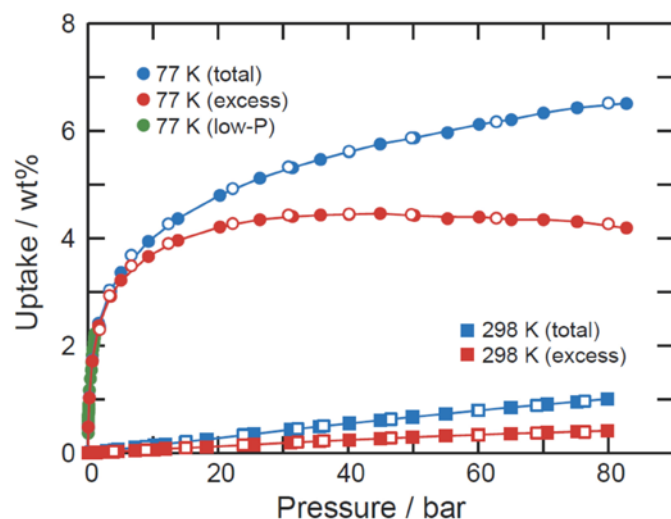


FIGURE 2. High-pressure H_2 isotherms of expanded Mg-MOF-74 at 77 K (red circles) and at 298 K (red squares). Calculated total uptake data were overlaid (blue symbols).

isotherm matches with the low-pressure data indicating that the measurements were properly carried out. Although the surface excess mass is a useful concept, the total amount that a material is able to store is more relevant to the practicality of using H_2 as a fuel. Therefore, we estimated this value by using a pore volume and bulk H_2 density ($N_{total} = N_{ex} + \rho_{bulk} V_p$). Estimated total H_2 uptake was plotted in Figure 2 (blue circles). Total uptake at 80 bar was calculated to be 6.5 wt%, which corresponds to 43 g/L. Due to the moderate BET surface area of expanded MOF-74, the total gravimetric uptake is not overwhelmingly exceptional. However, the volumetric uptake is well within the realm of the DOE system target albeit at 77 K.

We also measured H_2 isotherms of the same sample at 298 K (Figure 2). The excess uptake at 80 bar was 0.41 wt%, which was unfortunately smaller than the H_2 uptake at 87 K and 1 bar (1.5 wt%). This implies that a higher Q_{st} value is required to increase the H_2 density in MOFs even though the Q_{st} for expanded MOF-74 is ca. 10 kJ/mol. The estimated total H_2 uptake at 80 bar and 298 K was calculated to be 1.0 wt% (6.3 g/L). This volumetric uptake is slightly higher than the bulk density of H_2 at the same condition (6.2 g/L). In order to improve on these results, we plan to synthesize the isorecticular structures using Ni and Co ions instead, which are reported to have Q_{st} values greater than that of Mg-MOF [2].

Ultrahigh Porosity in MOF-200 and 210. One of the most important properties of MOFs is their high porosity and high specific surface area. An important consideration in maximizing the uptake of H_2 within MOFs is to increase the number of adsorptive sites within a given material. The simplest way to accomplish this is to use slim organic linkers in which the faces and edges of the constituent units are exposed for gas adsorption [3]. As shown in MOF-5 and MOF-177, the octahedral $Zn_4O(CO_2)_6$ (Figure 1C) has had a prominent role as a building unit in producing structures exhibiting exceptional porosity [1,3]. Therefore, we prepared the expanded forms of MOF-177 from 4,4',4''-(benzene-1,3,5-triyl-tris(benzene-4,1-diyl))tribenzoate (BBC) to give MOF-200, and used mixed 4,4',4''-(benzene-1,3,5-triyltris(ethyne-2,1-diyl))tribenzoate (BTE)/ biphenyl-4,4'-dicarboxylate (BPDC) links to obtain MOF-210 (Figure 1C).

MOF-200 and 210 were prepared from a solvothermal reaction of organic linkers and zinc nitrate, and obtained crystals were characterized single crystal X-ray diffraction. Considering the bulk density and void space calculated from the crystal structure analyses, MOF-200 and 210 are promising candidates to realize ultra-high surface area. However, preliminary trials revealed that the solvent exchange followed by pore evacuation under vacuum was not effective to activate MOF-200 and 210 without losing the porosity. Therefore, these crystals were fully exchanged with liquid CO_2 , kept under supercritical CO_2 atmosphere, followed by their pores being bled of CO_2 to yield activated samples. Successful guest removal was confirmed by PXRD measurements and elemental analyses.

As shown in Figure 3, these MOF samples show distinctive steps ($P/P_0 = 0.14$ and 0.27 for MOF-200 and 210), and the profiles for MOF-200 and 210 are nearly the same as the predicted isotherms by grand canonical Monte Carlo simulations (Prof. Snurr group at Northwestern University). The maximum N_2 uptake capacities at 77 K in MOF-200 and 210 are $2,340$ and $2,330 \text{ cm}^3 \text{ g}^{-1}$, respectively. More importantly, the measured values are near the values predicted based on the structure, indicating that these materials are well-activated. Because of the successful sample activation, extremely high BET (and Langmuir) surface areas were obtained: $4,530$ ($10,400$) and $6,240$ ($10,400$) $\text{m}^2 \text{ g}^{-1}$ for MOF-200 and 210. The BET surface area of MOF-210 is the highest reported for crystalline materials.

Given the exceptional properties of such materials, it is expected that these high surface area MOFs would exhibit exceptional H_2 storage capacity. These MOFs reach saturation uptakes, and the saturation pressure increases with an increase in the cavity size (Figure 4). The surface excess H_2 uptake in MOF-210 ($7.9 \text{ wt}\%$) was higher than MOF-177 and 200 (6.8 and $6.9 \text{ wt}\%$) [4]. Given the pore volume and density of H_2 at 77 K, the total H_2 uptake in MOF-210 is calculated to be $15 \text{ wt}\%$, which exceeds that of typical alternative fuels (methanol and ethanol) and hydrocarbons (pentane and hexane). MOF-200 also shows large total uptake ($14 \text{ wt}\%$); again, these values are higher than MOF-177 [4]. However, the volumetric total uptake (44 g/L for MOF-210; 36 g/L for MOF-200) was smaller than MOF-177 (50 g/L). The trend indicates that it is better to reduce the dead volume by introducing functionalities, which can interact positively with H_2 .

Figure 4 displays the room temperature H_2 isotherms of MOF-210. The excess uptake at 80 bar was $0.53 \text{ wt}\%$, which is similar to the room temperature H_2 uptake by MOF-177 ($0.54 \text{ wt}\%$). We believe that the excess H_2 uptake was not

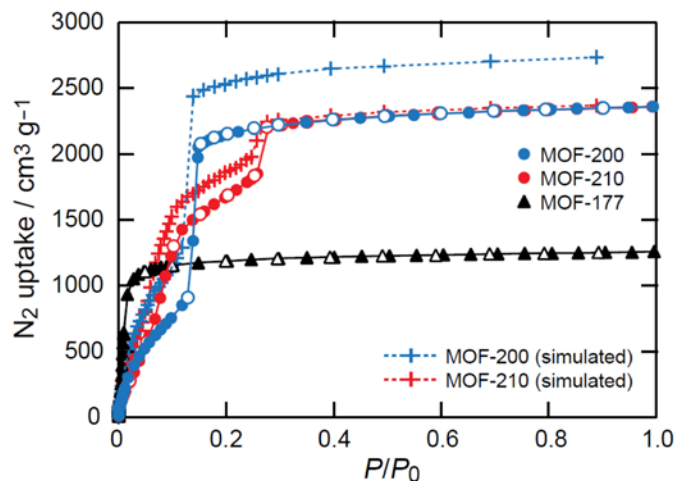


FIGURE 3. Low-pressure N_2 isotherms of MOF-177, -200, and -210 at 77 K. Simulated isotherms of MOF-200 and -210 were overlaid.

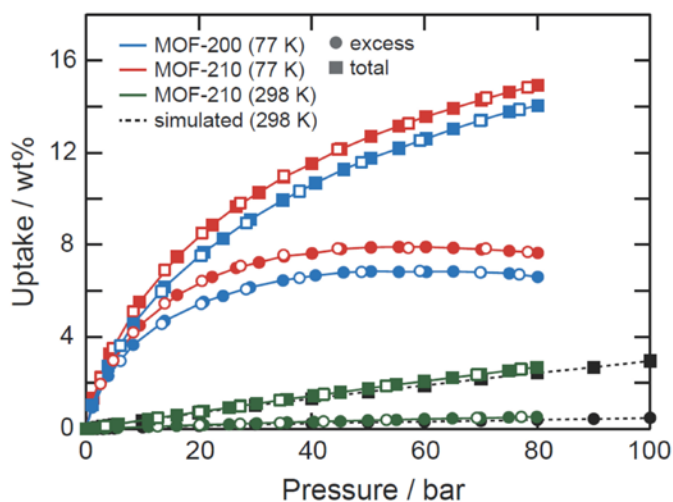


FIGURE 4. High-pressure H_2 isotherm of MOF-200 (blue circles) and 210 (red circles) measured at 77 K. Experimental (green) and simulated (black) H_2 isotherm of MOF-210 at room temperature are overlaid. Squares in the same color symbols represent calculated total uptake of H_2 under the same conditions.

improved because of the average pore diameter of MOF-210. The average pore diameter of MOF-210 is larger than the DOE recommendation for pore diameter size (0.7 - 1.2 nm to maximize the room temperature H_2 uptake capacity) with a significant storage space that still remains.

Calculated total H_2 isotherm is also shown in Figure 4. The total uptake at 80 bar was $2.7 \text{ wt}\%$, which is the highest number reported for physisorptive materials. When the bulk density of MOF is applied, the volumetric H_2 uptake is calculated to be 6.9 g/L at 80 bar. Although the majority of the total uptake is attributed to the large pore volume (i.e. the contribution from $\rho_{\text{bulk}} V_p$), the volumetric H_2 uptake by MOF-210 remains higher than the bulk density of H_2 under the same conditions. Worth noting is that this finding is in sharp contrast to the fact that MOFs with larger density typically show even smaller volumetric uptakes than the bulk H_2 density.

Through the collaborative work with the Prof. Goddard group of Caltech, room temperature H_2 uptake by MOF-210 was predicted. As shown in Figure 4, these room temperature high-pressure H_2 data are in good agreement with predicted excess and total isotherms. However, H_2 isotherms recorded at room temperature sometimes contain significant errors due to their smaller uptake (compared to 77 K data). Therefore, it is fair to say that the simulation data provides reassuring support for the excellent experimental room temperature H_2 uptake capacity by MOF-210.

Conclusions and Future Directions

In this project, we aimed at developing the next generations of MOFs. It is presumed that the organic functionalities alone were not enough to show strong

binding energy, therefore, we prepared novel MOFs with metals. These MOFs showed improved adsorption enthalpy albeit a large pore volume is still a prerequisite feature. From the viewpoint of the storage space, we aimed at discovering high surface area MOFs. After many trials we optimized the synthesis and subsequent activation conditions of MOF-210, leading to 15 and 2.7 wt% of total H₂ uptake at 80 bar at 77 and 298 K, respectively. Although this project has finished, we will continue to pursue practical storage targets by the combination of the isoreticular metalation and the isoreticular expansion.

Special Recognitions

1. The 2010 Centenary Prize from the Royal Society of Chemistry.

FY 2011 Publications

1. H. Furukawa, N. Ko, Y.B. Go, N. Aratani, S.B. Choi, E. Choi, A.O. Yazaydin, R.Q. Snurr, M. O’Keeffe, J. Kim, O.M. Yaghi, “Ultra-High Porosity in Metal-Organic Frameworks,” *Science*, **329**, 424-428 (2010).
2. D. Britt, C. Lee, F.J. Uribe-Romo, H. Furukawa, O.M. Yaghi, “Ring-Opening Reactions within Porous Metal-Organic Frameworks,” *Inorg. Chem.*, **49**, 6387-6389 (2010).

3. S. Barman, H. Furukawa, O. Blacque, K. Venkatesan, O.M. Yaghi, and H. Berke, “Azulene Based Metal-Organic Frameworks for Polarized Binding of H₂,” *Chem. Commun.*, **46**, 7981-7983 (2010).
4. D. Britt, “Metal-Organic Frameworks for Gas Separation,” University of California - Los Angeles, 2010, Ph. D. thesis.
5. E. Choi, “The Construction of Metal-Organic Framework with Active Backbones by the Utilization of Reticular Chemistry,” University of California - Los Angeles, 2011, Ph. D. thesis.

References

1. J.L.C. Roswell, O.M. Yaghi, *J. Am. Chem. Soc.*, **128**, 1304 (2006).
2. W. Zhou, H. Wu, T. Yildirim, *J. Am. Chem. Soc.*, **130**, 15268 (2008).
3. H.K. Chae, D.Y. Siberio-Perez, J. Kim, Y.-B. Go, M. Eddaoudi, A.J. Matzger, M. O’Keeffe, O.M. Yaghi, *Nature*, **427**, 523 (2004).
4. H. Furukawa, M.A. Miller, O.M. Yaghi, *J. Mater. Chem.*, **17**, 3197 (2007).