IV.C.4 Hydrogen Storage in Metal-Organic Frameworks

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Objectives

- Implementation of "soft chemisorption": design and preparation of new metal-organic framework (MOF) with metal binding sites:
    – Impregnation of metals.
    – Low-pressure measurements at various temperatures.
- Preparation of high-surface area MOFs for isoreticular covalent organic functionalization:
    – Preparation of expanded organic link.
    – High-throughput MOF synthesis.
- Coordination with theory:
    – Prediction of binding energy.

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

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 revised DOE 2015 hydrogen storage targets:

- Volumetric density: 40 g L^{-1}
- Gravimetric density: 5.5 wt%

Accomplishments

- Synthesized new Al and Zr-MOFs with bipyridine links for isoreticluar metallation.
- Developed aziridation reactions to introduce ethanediamine group ($-NHCH_2CH_2NH_2$) on newly prepared MOFs with amino groups.
- Began metal-doping experiments for immobilization of metal complexes.
- Environment of the metal coordination sites was studied by the extended X-ray absorption fine structure spectroscopy (EXAFS).
- Applied supercritical CO_2 drying technique for sample activation.
- Crystalline material with the lowest density as observed was prepared.

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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 H_2 storage; 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 show that 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 2015 system targets by physisorption, adsorbents must have high surface area (>3,000 m^2 g^{-1}) and relatively high density (>0.70 g cm^{-3}). We have already demonstrated how to design high

surface area materials; however, in many cases these materials do not show steep H_2 uptake in the low pressure region, which is indicative of the weak interaction with H_2. Last year, based on the relationship between adsorption enthalpy and Henry's constant, we suggest 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 we believe that metal impregnation is one of the most promising strategies. At present there are at least two challenges that must be addressed for a porous MOF with strong H_2 binding sites to be realized. The first is to create metal binding sites in the MOF structures; second is characterization of coordination behavior of metals in the frameworks. In this year we prepared MOFs possessing metal binding sites by different methods. In one case we employed functionalized organic links to immobilize metal ions; in another isoreticular functionalization was used to create potential metal binding sites. These MOFs were used for successive metal impregnation experiments.

Synthesis of MOFs with Bipyridine Links – We prepared new Al- and Zr-MOF with 2,2'-bipyridine-5,5'-dicarboxylate (BPyDC) link by solvothermal synthesis. The reasons why we chose these systems are as follows: (i) two nitrogen atoms in the organic link can hold metals, while these metals do not form small molecules (e.g. M(BPy)$_3$), (ii) higher stability compared to Zn-MOFs, (iii) simple and scalable synthetic procedure, (iv) prevention of metal exchange during the metal impregnation process, and (v) relatively long ditopic link is advantageous for providing reasonable surface area and pore volume even after the metal impregnation.

The structure of Al-MOF ([Al(OH)(BPyDC)], termed MOF-253) was confirmed by powder X-ray diffraction measurements and elemental analysis. The Brunauer-Emmett-Teller (BET) surface area is calculated to be 1,380 m^2 g^{-1}, and its H_2 uptake at 77 K and 1 bar is 14 mg g^{-1}. To implement metal impregnation, pristine MOF-253 was immersed in the solution containing Sc(III) ion. After washing unreacted metal ions and successive drying, N_2 and H_2 isotherms were recorded for the resulting compound, termed MOF-253-Sc. As shown in Figure 1, the profile of the H_2 isotherm for MOF-253-Sc is almost the same as the pristine material, indicating that metal ions are not immobilized. Indeed, the inductively coupled plasma analysis supports this result. Next, we tried a similar impregnation reaction with excess Cr(III) and Fe(III) ions. In order to avoid leaching of metals, we only used a small amount of
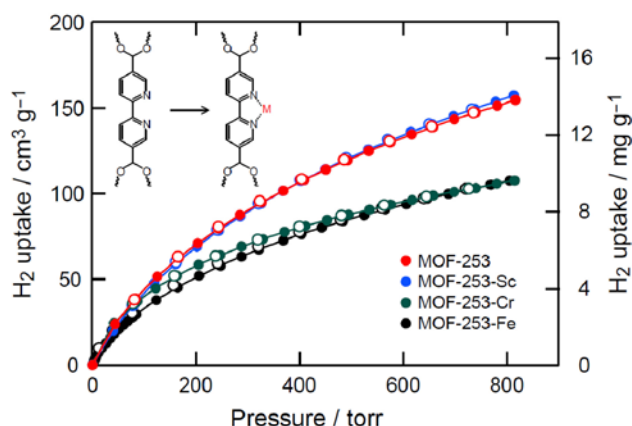

FIGURE 1. Low pressure H_2 isotherms for MOF-253 and its derivatives at 77 K. (Inset) proposed metallation reaction in MOFs.

solvent to wash the sample (MOF-253-Cr and MOF-253-Fe, respectively). The H_2 isotherms for MOF-253 derivatives are illustrated in Figure 1. Although slight color change for the MOF was observed, metal salts contaminated the sample (by visual observation). Therefore, it is difficult to compare the H_2 uptake capacity of this sample to pristine MOF-253. However, given the profile of the isotherm, it doesn't seem that the Henry's constant of the isotherm is improved drastically. We will impregnate other metals such as Pt and Pd to study H_2 uptake behavior.

When ZrCl$_3$ was used as a metal source, Zr-MOF (Zr$_6$O$_4$(OH)$_4$(BPyDC)$_6$, termed MOF-267) was obtained. From the similarity of the powder X-ray diffraction patterns, it is presumed that the connectivity of MOF-267 is the same as UiO-67 [1]. The calculated BET surface area is 1,550 m^2 g^{-1} and H_2 uptake at 77 K and 1 bar was 11 mg g^{-1}. We plan to perform the metal impregnation experiments in the next fiscal year.

Impregnation of Ethanediamine-MOF with Metal Ions – Originally we prepared IRMOF-3 derivatives having ethanediamine group (-NHCH$_2$CH$_2$NH$_2$, terms IRMOF-3n) by isoreticular functionalization. After the modification, IRMOF-3n was immersed in the solution containing Fe(II) ions. However, the metal composition of the IRMOF-3 derivative implies that zinc ions leached out from the IRMOF and were coordinated to ethanediamine groups. Therefore, we prepared the analogous Al-based MOF ([Al(OH)(NH$_2$-BDC)], MOF-153) to prevent unexpected side reactions. Indeed, in our preliminary analyses, MOF-153 shows higher thermal and chemical stability compared to IRMOFs, even though the surface area is not quite as high.

Addition of the ethyleneamine group was performed in toluene with excess amount aziridine. After the reaction the powder X-ray diffraction pattern was similar to the original material. We further characterized the post-modified materials by nuclear magnetic resonance

and elemental analysis. Unlike IRMOF-3, it seems that the aziridine reaction didn't occur in the cage of MOF-153. This result may be due to the smaller pore diameter of MOF-153 compared to IRMOF-3. Therefore, we prepared a new amino-functionalized MOF with larger cavity (termed MOF-202).

The topology (connectivity) of MOF-202 is the same as MIL-101 [2]. Since MOF-202 has large pore openings (>10 Å) and two types of large cages (25–30 Å), we expected that the pore aperture/diameter of MOF-202 after the reaction with aziridine would remain large enough for gas diffusion. However, the BET surface area of MOF-202n (modified material) was much smaller than that of the pristine material (2,000 and 525 m^2 g^{-1} for MOF-202 and MOF-202n, respectively). The reason for the surface area decrease is not clear. Considering that powder X-ray diffraction pattern of MOF-202n is identical to MOF-202, pore openings of MOF-202n could be partly blocked by the post-modification process. We also saw by mass spectra that we had multiple additions of ethyleneamine to a single terminal amine group, resulting in an oligomer.

After modification, MOF-202n was immersed in a solution containing Cr(III) ions. Hereafter, the Cr-treated sample is termed MOF-202n-Cr. The BET surface area of MOF-202n-Cr was estimated to be 200 m^2 g^{-1}, which is smaller than MOF-202n probably due to the mass added as a result of metal impregnation. Figure 2 illustrates the H_2 isotherms for MOF-202n and MOF-202n-Cr measured at 77 K. The metal impregnated material shows slightly better H_2 uptake behavior in the very low pressure range; however, adsorbed H_2 amount in these MOFs are much smaller than in the pristine sample (MOF-202). This deficit indicates that higher surface area is a prerequisite for the reasonable H_2 uptake.

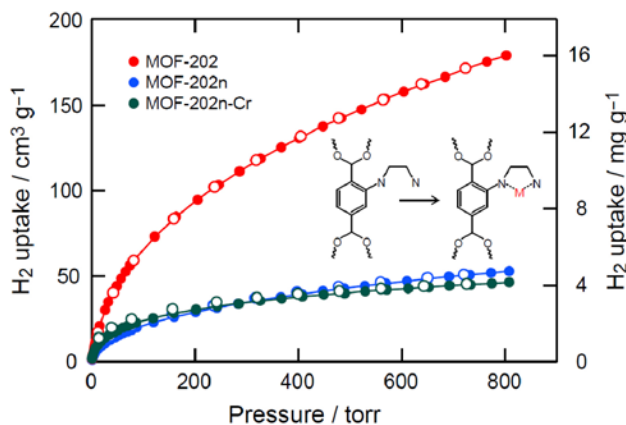Based on the 77 and 87 K isotherms, the heat of adsorption (Q_{st}) of H_2 was estimated. Unexpectedly, the impregnated compound shows smaller Q_{st} value (7.1 kJ mol^{-1}) compared to MOF-202n (9.9 kJ mol^{-1}), indicating that there is no strong Cr-H_2 interaction in this system. We heated the sample at 200°C for 2 days to remove any solvent occluded in the pores. However, the profile of the H_2 isotherm for MOF-202n-Cr didn't change even after heating. Although it is not clear whether there are solvent molecules on Cr ions, it seems that heating is not an effective method for activation. It may be necessary to extract coordinated solvents under supercritical conditions (e.g. CO_2).

Isoreticular Metallation of MOFs – Although metal impregnation experiments were performed using two new MOFs, it is still not clear how the metals were bound to organic functionalities. The lack of the information on the metal coordination sites may hamper understanding of any metal-H_2 interaction. We chose another MOF system (($Zn_4O)_3(NH_2$-BDC)$_3$(BTB)$_4$) to implement the isoreticular covalent modification and successive metallation (Pd coordination). Indeed, after reaction with a palladium salt, almost 100% of metal coordination sites were occupied by palladium ions. In general it is not easy to determine the metal coordination environment within the framework based on elemental analysis and conventional X-ray diffraction techniques. Therefore, the metal coordination environment was investigated by Pd K-edge EXAFS.

Crystals of ($Zn_4O)_3(NH_2$-BDC)$_3$(BTB)$_4$ (Figure 3, **A**), were reacted with 2-pyridinecarboxaldehyde to form the covalently bound iminopyridine chelate derivative, ($Zn_4O)_3(C_6H_5N_2$-BDC)$_3$(BTB)$_4$ (**B**), which was reacted with PdCl$_2$(CH$_3$CN)$_2$ to give the metal complexed MOF, ($Zn_4O)_3(C_6H_5N_2$PdCl$_2$-BDC)$_3$(BTB)$_4$ (**C**). Remarkably, these reactions and their respective products are achieved without loss of structural order or framework connectivity.
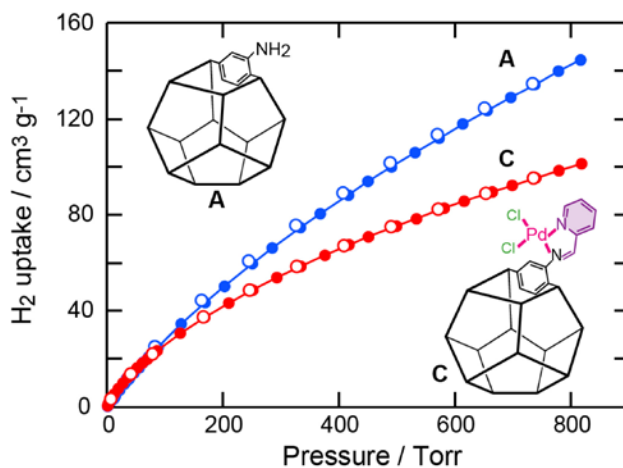

FIGURE 2. Low pressure H_2 isotherms for MOF-202 and its derivatives at 77 K. (Inset) proposed metallation reaction in the ethanediamine-MOF.

FIGURE 3. Low-pressure H_2 isotherms for compound **A** (blue) and **C** (red) measured at 77 K. Molecular structures of **A** and **C** (before and after functionalization, respectively) are shown as cage structures.

The porosity of **B** and **C** was confirmed by Ar adsorption measurements at 87 K (the BET surface areas for **B** and **C** are 3,200 and 1,700 $m^2 g^{-1}$, respectively). It is worth noting that both materials maintain porosity after two subsequent chemical transformations. Additionally, Type IV isotherms are observed in all samples (**A**-**C**). We also note that compounds **B** and **C** were activated on the supercritical CO_2 dryer, and no sample degradation under the supercritical conditions was observed. Based on repeated use for several compounds, we conclude that supercritical CO_2 drying is the best way to activate metal impregnated samples.

Figure 3 demonstrates low-pressure H_2 isotherms for compounds **A** and **C**. H_2 uptake in **C** is 0.9 wt% at 77 K and 1 bar, which is smaller than that in **A** due to the smaller BET surface area. However, the heat of adsorption profile for **C** is improved by metallation (the Q_{st} values at zero-coverage for **A** and **C** are 5.7 and 6.6 kJ mol^{-1}, respectively). The successful isoreticular covalent transformation followed by metallation opens a route for incorporating metal ions into a wide range of frameworks. This is an important first step toward exploiting such metallated frameworks in gas-storage applications.

Isoreticular Expansion of MOFs – Isoreticular covalent functionalization and metallation is a very important strategy to enhance hydrogen density at room temperature. However, we notice that preparation of larger pore MOFs is a prerequisite for implementation of isoreticular modification without reduction of surface area. Therefore, we designed and prepared expanded structures of MOF-177 and MOF-199 with much larger unit cell parameters than original structures without changing the underlying topology by employing a longer tritopic organic link (1,3,5-tris(4'-carboxy[1,1'-biphenyl]-4-yl-)benzene, H_3BBC).

MOF-200 ($Zn_4O(BBC)_2$) was prepared as truncated octahedral crystals by solvothermal reaction of H_3BBC and $Zn(NO_3)_2$. Because of the long organic link, the cavity in MOF-200 encloses a sphere of 2.2 nm. MOF-399 has even larger pore (4.5 nm in diameter), although the organic link is the same as MOF-200. MOF-399 was prepared solvothermally by employing H_3BBC and $Cu(NO_3)_2$, which resulted in blue-green truncated crystals. The calculated density for MOF-399 based on the single crystal data is 0.13 g cm^{-3}. This value is markedly lower than those of highly porous MOFs known previously, such as MOF-177 and 200 (0.43 and 0.23 g cm^{-3}, respectively). It should be noted that the density of MOF-399 is even lower than that of COF-108 (0.17 g cm^{-3}) [3], which is known as the organic crystal with the lowest density. Next year we will activate these expanded MOFs using the supercritical CO_2 dryer and examine their high pressure H_2 uptake behavior.

Conclusions and Future Directions

For room temperature H_2 storage, strong binding energy is a prerequisite. In the case of $(Zn_4O)_3(C_6H_5N_2PdCl_2\text{-}BDC)_3(BTB)_4$, the binding energy between metal and H_2 was improved by 15%; however, the reduction of surface area also reduces H_2 uptake capacity by 30%. This again raises the importance of high surface area materials. In the future we will perform isoreticular functionalization and metallation on high surface area MOFs to improve storage temperature of H_2.

- Employ light weight metals to create strong binding sites (e.g. potential halogen-lithium exchange).
- Use inorganic secondary building units with transition metals to create open metal sites.
- Material design based on theoretical prediction (design proximal Lewis acid-base sites).
- Supercritical CO_2 drying for ultrahigh surface area MOFs.

Special Recognitions & Awards/Patents Issued

1. The International Izatt-Christensen Award in Macrocyclic Chemistry to be presented at ISMC 2009.

2. Top 10 researchers in chemistry based on total citations.

3. ACS Award in the Chemistry of Materials.

FY 2009 Publications/Presentations

1. *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*, 11650-11661.

2. *Secondary building units, nets and bonding in the chemistry of metal-organic frameworks*, D.J. Tranchemontagne, J. L. Mendoza-Cortes, M. O'Keeffe, and O. M. Yaghi, *Chem. Soc. Rev.* **2009**, *38*, 1257-1283.

3. *Isoreticular Metalation of Metal-Organic Frameworks*, C.J. Doonan, W. Morris, H. Furukawa, O.M. Yaghi, *J. Am. Chem. Soc.*, **2009**, *131*, 9492-9493.

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, *Inorg. Chem.* to be submitted.

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