

IV.F.1 A Joint Theory and Experimental Project in the Synthesis and Testing of Porous COFs for On-Board Vehicular Hydrogen Storage

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(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

This project consists of conducting fundamental studies of COFs. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2015 hydrogen storage targets:

- Volumetric density: 40 g L⁻¹
- Gravimetric density: 5.5 wt%

Accomplishments

- Build high-throughput preparation setups.
- Develop structural determination technique using ab initio charge-flipping method.
- Synthesis of new COFs through hydrazone condensation.
- Began modeling study for optimal binding energy.



Objectives

- Synergistic work between Yaghi (UCLA) and Goddard (California Institute of Technology [Caltech]).
- Build high-throughput preparation setups for covalent-organic framework (COF) synthesis (high temperature and pressure).
- Develop chemistry to realize stable frameworks.
- Introduce potential metal binding sites through the COF synthesis.
- Determine atomistic connectivity of COFs using an ab initio charge-flipping method using powder X-ray diffraction (PXRD) data.
- Predict adsorption enthalpy of H₂ on various metal sites.

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

Introduction

Storage of hydrogen in porous materials is a promising approach to achieve the DOE system requirements for use of hydrogen as a transportation fuel. Since the first report of successful hydrogen storage in metal-organic frameworks (MOFs), we and others have succeeded in incrementally increasing the gravimetric and volumetric capacities to reach the highest hydrogen uptake capacity, albeit at 77 K. However, for on-board vehicular hydrogen storage it is necessary to improve the adsorption enthalpy of porous materials to achieve significant capacities at room temperature. 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 MOFs and COFs; however, in many cases, these materials do not show steep H₂ uptake in the low pressure region indicative of the weak interaction with

H_2 . It is predicted that the impregnation of COFs with metals should enhance the adsorption enthalpy; therefore, we explore methods for the preparation of metalated COFs using high-throughput techniques. In this fiscal year, we developed a new class of COFs for metal impregnation and applied an ab initio charge-flipping method for structural analysis.

Results

Metal impregnation is one of the most promising strategies to improve the adsorption enthalpy of COFs. However, before the metal impregnation experiments, it is necessary to prepare stable COFs, and it is preferable to introduce metal binding sites in the framework through the condensation reaction. To this end, we designed and prepared new COFs having hydrazone and imine moieties. In addition, we applied a new technique to the structural analysis of COFs, which can be useful in determining the structure from low-resolution PXRD data. With regard to the simulation calculations, we demonstrated a method based on accurate quantum mechanics that allows us to screen different metal complexes to determine the enthalpy of adsorption at 298 K and 1 atm. We proposed a way to tune the H_{ads} based on the degree of metalation of our linkers.

1. Synthesis of Crystalline Hydrazone COF (UCLA)

We have developed the synthesis of new COFs constructed from the dehydration of aromatic carbohydrazides and aldehydes to form carbohydrazones (Figure 1A). This functional group shows interesting features such as the presence of both of amides and imines, resulting in materials with high thermal and chemical stability as well as dynamic reversibility forming libraries of polymers that exchange monomers in solution; moreover, hydrazones possess both carbonyls and nitrogen atoms that can be available for metal coordination/impregnation. An additional advantage for the synthesis of hydrazone-based materials is the easy synthesis of the hydrazone building blocks, which are prepared from the condensation of hydrazine and a carboxylic acid ester in refluxing alcohols with high yields.

A new COF, termed COF-41 was crystallized by reacting terephthalohydrazide with 1,3,5-tris(4-formylphenyl)-benzene through solvothermal conditions in mesitylene/dioxane/acetic acid/water mixtures (Figure 1A). The formation of the hydrazone linkages was determined by solid state Fourier transform infrared (FTIR) and ^{13}C nuclear magnetic resonance (NMR) of synthesized COF-41, starting materials, and model compound *N*'-benzylidene-benzohydrazide. The FTIR spectrum of COF-41 shows the characteristic C=N vibrational modes at 1,558 and 1,273 cm^{-1} (1,550 and 1,288 cm^{-1} in model compound). The solid-state

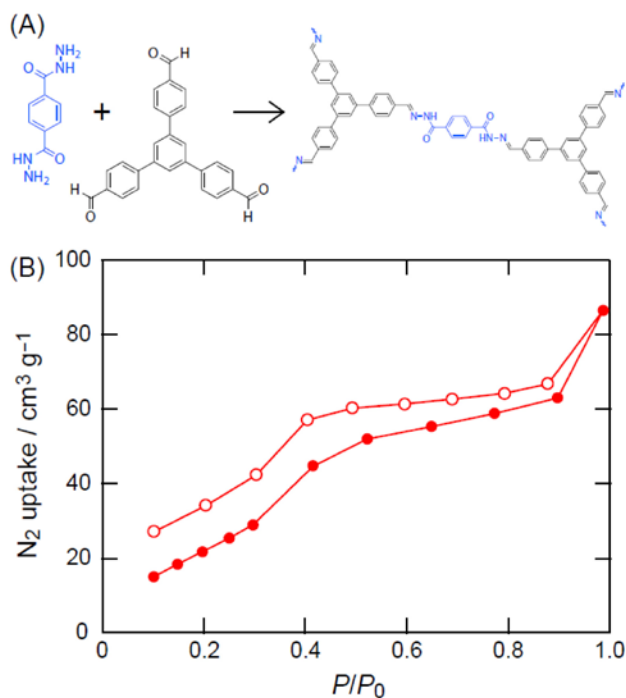


FIGURE 1. (A) Reaction scheme for the synthesis of COF-41. (B) N_2 isotherm for COF-41 at 77 K.

^{13}C NMR spectrum shows a chemical shift for the C=N of 149.2 ppm, compared to shifts of 150.2 ppm for the model compound and 192.5 ppm for the aldehyde in the starting material. The crystallinity of COF-41 was confirmed by PXRD from which the diffraction peaks were indexed into a primitive hexagonal unit cell ($a = 43.52 \text{ \AA}$, $c = 3.62 \text{ \AA}$) and compared to simulated patterns from crystal models of hexagonal layers packing in **bnn** (eclipsed) and **gra** (staggered) topologies.

In order to ascertain the correct structure, we performed porosity studies in which information such as surface area and pore size distribution will confirm one structural model or another. Preliminary porosity measurements on COF-41 (Figure 1B) give the Brunauer-Emmett-Teller (BET) surface area of $110 \text{ m}^2 \text{ g}^{-1}$ with a Type IV isotherm, characteristic of a mesoporous material. It seems that the obtained surface area was smaller than that of ideal value; therefore, we plan to optimize the synthetic and sample activation conditions.

2. Synthesis of Porphyrin Containing COF (UCLA)

In the pursuit for the preparation of a material in which different metals can be inserted, we are exploring the synthesis of COFs containing porphyrin rings. Porphyrin is a well-defined molecule and much effort has been devoted to study nature of metal substituted porphyrins. Therefore, we implemented the imine condensation of tetra(4-aminophenyl) porphyrin with terephthalaldehyde to obtain a new

porphyrin COF (termed COF-366, Figure 2A) whose condensation manor is the same as COF-300 [1]. COF-366 was prepared by the following procedure: tetra(4-aminophenyl) porphyrin and terephthalaldehyde in a solvent mixture of ethanol/mesitylene/acetic acid were placed in a pyrex tube. The tube was sealed at 77 K and under vacuum, and heated at 120°C for three days. The obtained purple powder was washed with absolute ethanol and immersed in anhydrous tetrahydrofuran for 24 h. The solvent was removed under vacuum at room temperature, yielding a porous material (yield: 79% based on the porphyrin).

A PXRD pattern of COF-366 showed an intense peak at 3.5° matching the unit cell of the simulated crystal, indicating that the distance between neighboring porphyrin rings is roughly 25.6 Å. It is likely that the connectivity of obtained COF has a **sql** topology (i.e. 4,4-grid type layered material). However, it is not clear if the layers are piled by an eclipsed fashion based on the PXRD data. We will discuss this point later in conjunction with gas adsorption measurements.

This solvent exchanged sample was activated on a supercritical CO₂ dryer to obtain porous crystalline solids. The Langmuir and BET surface areas of COF-366 were estimated based on the N₂ isotherm

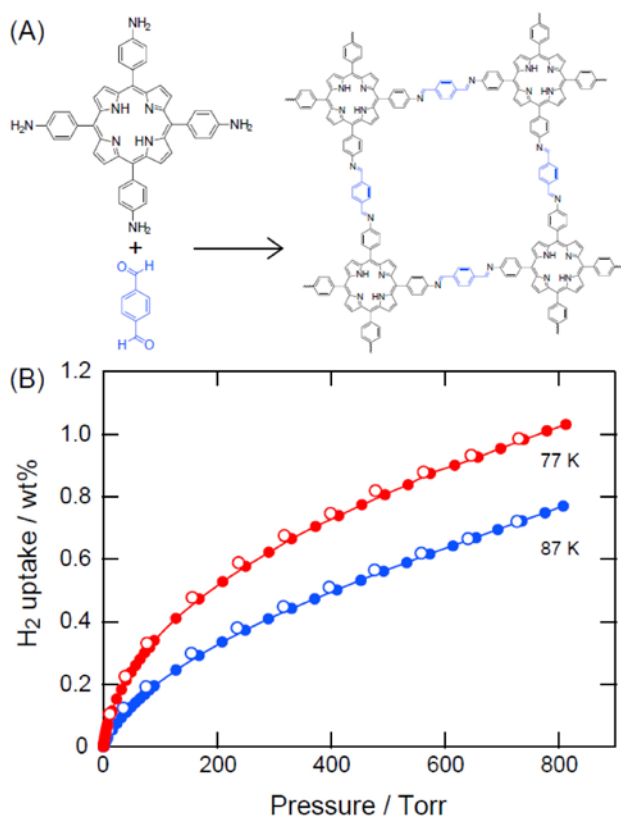


FIGURE 2. (A) Reaction scheme for the synthesis of COF-366. (B) H₂ isotherms for COF-366 at 77 K (red) and 87 K (blue).

measured at 77 K (1,270 and 990 m² g⁻¹, respectively). It should be noted that the profile of the isotherm is classified into Type I. If the sample has a one-dimensional channel, the isotherm should show a significant step around $P/P_0 = 0.1$ to 0.2, because the distance between neighboring porphyrins (>20 Å) will be large enough to cause micropore filling of N₂. The lack of step in isotherms implies that the porphyrin layers are staggered, leading to the micropore. We also tested low-pressure H₂ uptake capacity for COF-366 (Figure 2B). The H₂ uptake at 1 bar and 77 K is 1.0 wt%. Based on the 77 and 87 K isotherms, the Q_{st} was estimated. Calculated Q_{st} at the zero coverage (6.6 kJ mol⁻¹) is better than other COFs (COF-1, 5, 10, 102, 103) except COF-6 (7.0 kJ mol⁻¹). To improve the number, we plan to perform a metalation reaction.

3. Pore Structure from Low-Resolution PXRD Data (UCLA)

One of the difficulties in the COF projects is precise structure determination. Since COFs are synthesized by a condensation reaction of organic materials, it is possible to predict the connectivity of these building units. However unlike MOFs, COFs are comprised of light elements; therefore, obtained PXRD patterns may not provide enough diffraction lines and resolutions to resolve the structure. Indeed, we have encountered the problem when we prepared COF-300 [1]. Recently, ab initio charge-flipping method was developed [2,3]. In this method, unit cell parameters are required (i.e. hkl indices with intensity); while no information related to the connectivity and space group is necessary. Since it can be possible to determine the atomistic connectivity based on the PXRD data, we applied this technique to solve the COF structure.

Originally, we tried to solve the structure of as-synthesized COF-300, because the degree of interpenetration is not clear. However, due to the disordered solvent molecules, we could not obtain meaningful result. Therefore, we used activated COF-300. Figure 3 demonstrates the PXRD pattern of COF-300. We refined the pattern with 2-Å resolution. Using obtained hkl information (including intensity of each diffraction), electron density map was generated on *Superflip* [3]. Figure 3 (left) demonstrates the electron density map for COF-300 along the *c*-axis. As we expected, square channel was observed, and the dimension of the pore is almost identical to the space filling model of COF-300.

For the structure determination, reasonable resolution (preferably shorter than bond distance) and intense diffraction lines (at least 10 lines, although it depends the space group) are required. So far, we could not solve COF-366 structure due to the insufficient X-ray diffraction pattern. However, we believe that

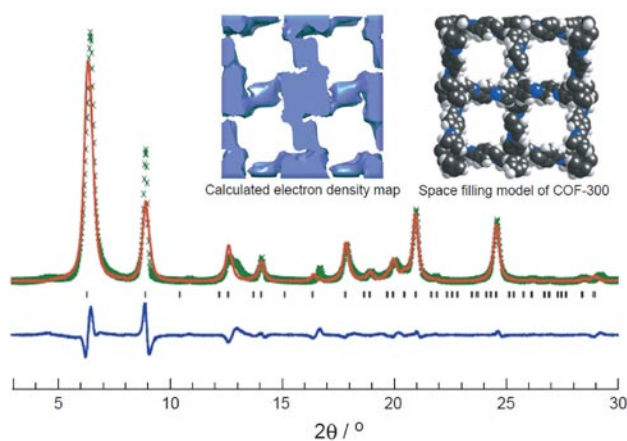


FIGURE 3. PXRD pattern of COF-300 (red), refined profile (green), and the deviation (blue). (Inset) Calculated electron density map (left) and space filling model (right) of COF-300.

pore structure should be revealed when a better PXRD pattern is obtained.

4. Interaction Energies for Imine COFs (Caltech)

We performed ab initio quantum mechanics to investigate the interaction of the H_2 molecules with different building blocks for potential COFs. We decided to use density functional theory (DFT) at M06 level which has been shown to predict accurately interaction energies for non-covalent interactions [4,5] including that of H_2 . We used the algorithm as implemented in Jaguar 7.0 [6] using the LACVP basis set.¹

We chose the structures shown in Figure 4, because we found similar building blocks in the literature that have been synthesized and are reported in the Cambridge structural database [7]. We chose the metals in the light on the easiness of synthesis and handling; such as, Cu, Pt, Cu, and Zn. We also propose to use some other lighter early transition metals like Cr, Mn, Fe, Co, and Ni that given the lighter mass character can help us in gravimetric units. The reasoning behind selection of such targets is that we want the metal site to interact as direct as possible with H_2 molecules, so we chose metal that can form square planar or tetrahedral geometries.

Using our DFT-MO6 method we calculated the adsorption enthalpy (H_{ads}) at 298 K and 1 atm (Figure 4, right). From these calculations, the best performers are Cu, Ni, Pt, Co, and Zn (i.e., Models P, N, G, A, and J, respectively). The H_{ads} of these complexes are greater

¹ A basis set in chemistry is a set of functions used to create the molecular orbitals, which are expanded as a linear combination of such functions with the weights or coefficients to be determined.

than 15 kJ/mol, but these values are still below threshold interaction energy for an optimal H_2 adsorption.

It is worth noting that the degree of metalation is directly related to the value of H_{ads} . This can be seen when we compare similar models such as: B vs. F, C vs. G. This is more obvious when comparing D vs. E and L vs. P, where the H_{ads} increased by roughly 5 and 10 kJ/mol, respectively. Considering that the similar trend (addition of more metals to the complex improves the H_{ads}) is presented in other systems, it can be said that the H_2 near the metal complexes is stabilized by metals. This behavior can be potentially used to tune the H_{ads} and obtain a desirable system with the adequate degree of soft chemisorption. We can keep increasing our H_{ads} in systems such as models I to P.

Conclusions and Future Directions

This year we experimentally demonstrated how to connect di-, tri-, and tetra-topic building units through condensation reactions (i.e. hydrazone, imine, and boronate COFs). Since the atomistic connectivity and pore structure can be predicted based on the reticular concept, we plan to find candidates for metalation reactions of COFs through modeling studies. In addition, we will predict the binding energy between H_2 and metal unit.

- Material design assisted by the reticular synthesis.
- Theoretical prediction of the binding energy between H_2 and metalated COFs.
- Employ metals to create strong binding sites.
- Supercritical CO_2 drying to optimize the porosity.

Special Recognitions & Awards/Patents Issued

1. The 2010 Centenary Prize from the Royal Society of Chemistry.
2. The 2009 Izatt-Christensen Award.
3. Three of world's leading chemistry scholars in UCLA.

FY 2010 Publications/Presentations

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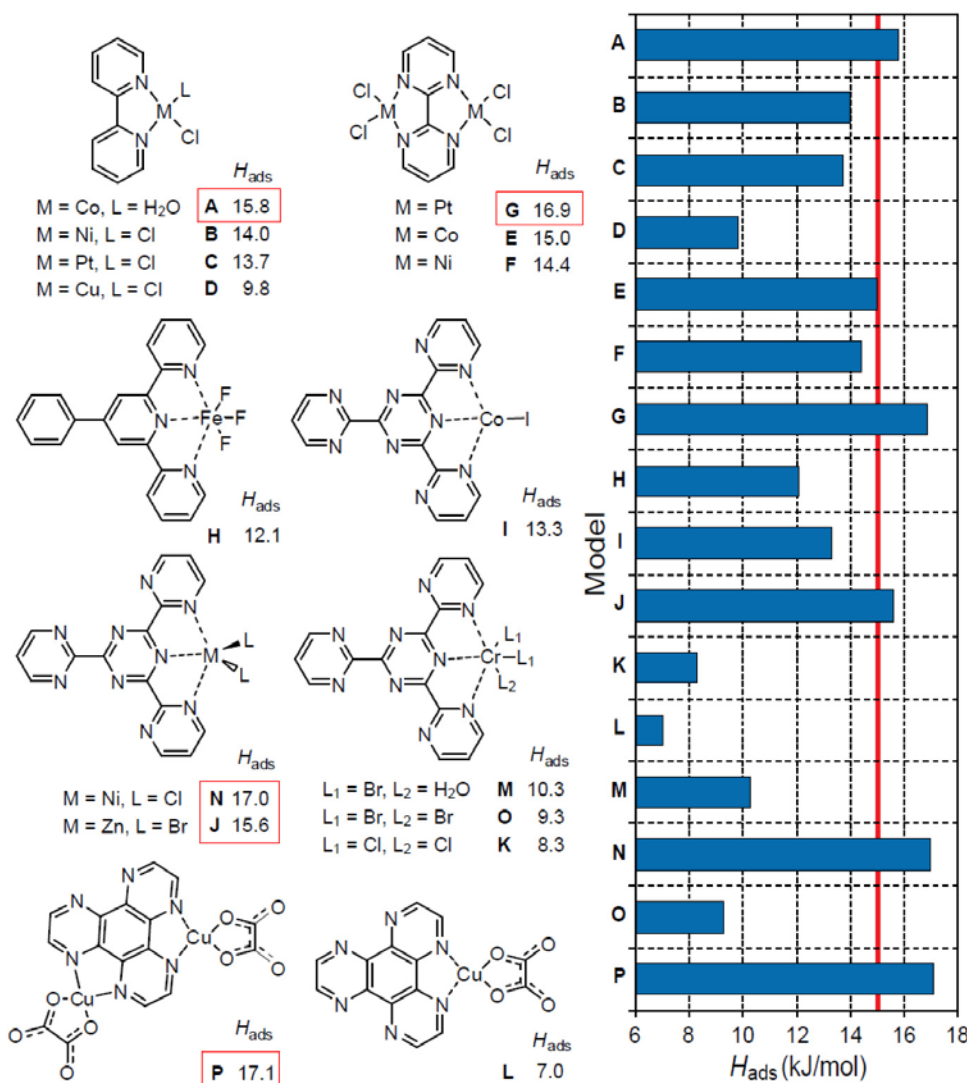


FIGURE 4. Model structures used for H_{ads} calculation. The red line indicates the 15 kJ/mol threshold.

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