IV.C.2 A Joint Theory and Experimental Project in the Synthesis and Testing of Porous COFs for Onboard Vehicular Hydrogen Storage

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Fiscal Year (FY) 2012 Objectives

- Design optimal frameworks with potential metal binding sites for metal impregnation.
- Predict H_2 uptake isotherm for designed frameworks using our newly developed force field.
- Implement metalation experiments and evaluate the H_2 adsorption property.
- Synthesize new covalent organic frameworks (COFs) with ultra-high surface area (>5,000 m^2 g^{-1}).

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

(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

This project consists of several fundamental studies on 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%

FY 2012 Accomplishments

- Synthesized new air stable COFs through imine condensation (COF-320 and 340).
- Performed metalation experiments of COFs (COF-301, phenanthroline-COFs).
- Synthesized two low density COFs with triptycene unit (0.15-0.21 g cm^{-3}).
- Predicted binding energy with different first row transition metals.
- Predicted H_2 isotherms and Q_{st} values of metalated COF-322, 330 and 333 (298 K, up to 100 bar).

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Introduction

Storage of hydrogen in porous materials is a promising approach to achieve the DOE system requirements for use of H_2 as a transportation fuel. After the first report of successful H_2 storage in metal-organic frameworks (MOFs), the Yaghi group has succeeded in incrementally increasing the gravimetric and volumetric capacities in order to to reach the highest H_2 uptake capacity, albeit at 77 K. However, for onboard vehicular H_2 storage it is necessary to improve the adsorption enthalpy of porous materials to achieve significant capacities at room temperature. Therefore, we are currently focusing our efforts on discovering highly porous materials with strong affinity for H_2.

Approach

To meet the DOE 2015 revised targets by physisorption, adsorbents must have high surface area (>3,500 m^2 g^{-1}) and relatively high density (>0.75 g cm^{-3}). We have previously demonstrated how to design high surface area MOFs and COFs [1]. However, in many cases, these materials do not show steep H_2 uptake in the low-pressure region, because

the binding energy based on non-covalent interactions (electrostatic and dispersion) is generally smaller than 10 kJ mol^{-1} [2,3]. In contrast, it is known that orbital interaction (i.e. the interaction between hydrogen and the d-orbital of transition metals) is stronger than van der Waals interaction, where the values may be greater than 20 kJ mol^{-1}. This prompts us to prepare COFs with metal binding sites and to impregnate COFs for the enhancement of the adsorption enthalpy. From the preliminary metal impregnation experiments, it seems that larger pore materials are better to implement the metal impregnation because metals and metal salts are solvated. In this year, we prepared expanded version of COF-300 with metal binding sites. In parallel with the synthesis, H$_2$ loading curves for the pristine and metalated COF materials were calculated.

Results

Metal impregnation is one of the most promising strategies to improve the adsorption enthalpy of COFs. However, our initial attempts at COF-301 indicate poor metalation yield. A similar problem was also observed in MOFs that have potential metal binding sites in their structures. Possible explanations for the low metalation yield include (1) low coordination ability of metal ions, (2) unfavorable conformation of the metal binding sites (i.e. a bipyridine linker can rotate), (3) steric hindrance due to the solvation of metal salts and the presence of counter anions, and (4) structural decomposition of the frameworks. Because the bipyridine moiety in the framework structure can rotate, it is likely that relatively large pore volume (large pore diameter) is critical to successful incorporation of the guest metal, which was not considered in simulation calculations. Before the metal impregnation experiments are carried out, it is necessary to prepare COFs with large pores. To this end, we designed and prepared expanded versions of COF-300 by condensation reactions.

Preparation of imine COF and its metalation reaction. We have demonstrated the condensation of the tetrahedral building block tetra-(4-anilyl)methane (Figure 1, **1**) with the linear linking unit terephthaldehyde (**2**) to produce a material with an extended three-dimensional framework structure (COF-300) [4]. To increase the storage space in COF materials, expansion of linker 2 is a good approach. Therefore the structures of organic linkers that can be easily synthesized and/or commercially available were investigated. It is intuitively found that linker **7** is a good candidate to expand the pore while introducing the potential metal binding sites. However, it is difficult to add aldehyde groups to the 3 and 8 positions. It could be possible to make linker **5** according to a literature procedure, but our final decision rather was to synthesize linker **6** due to the greater density of potential metal binding sites compared to **5**. In addition, the preparation of an expanded version of phenanthroline linker (**8**) was synthesized.
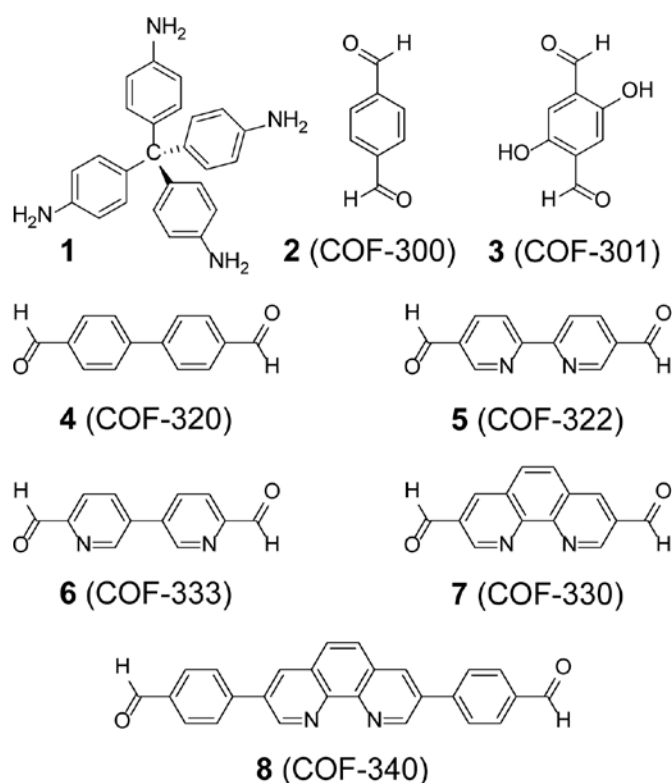

FIGURE 1. Molecular structures of tetratpoic (**1**) and ditopic building units (**2-8**), which form COF materials. The name of each COF is shown in parentheses.

The synthesis of COFs was carried out by solvothermolysis of a suspension of linker **1** and ditopic linker (**4**, **6**, or **8**) in a mixture of organic solvents. For a comparison of the porosity, a new COF (COF-320) using linker **4** was also newly synthesized. Synthetic conditions of these COFs were similar to COF-300, but these conditions are not optimized yet. Typically, a mixture of 1,4-dioxane and aqueous acetic acid with starting materials were heated at 120°C. All resulting materials are insoluble in water and common organic solvents such as: hexanes, methanol, acetone, tetrahydrofuran, and *N,N*-dimethylformamide. Therefore, the resultants are an extended structure.

The crystallinity of COF-320 and 340 was confirmed by powder X-ray diffraction (PXRD) analysis (Figure 2, top). Although its atomistic connectivity (including the degree of interpenetration) is not determined yet due to the limited numbers of diffraction peaks, it is important to note the position of the first peak located at lower angle when extended linkers were employed. This clearly demonstrates the successful pore expansion. Assuming that the connectivity (topology) of these COFs is in a diamond net, it is possible to build modeled structures (Figure 2, bottom). The simulated PXRD patterns are similar to those of experimental data, so that the full refinement of these COF will be performed in the future. With regard to COF-333, the solid material did not diffract well; although there are a few
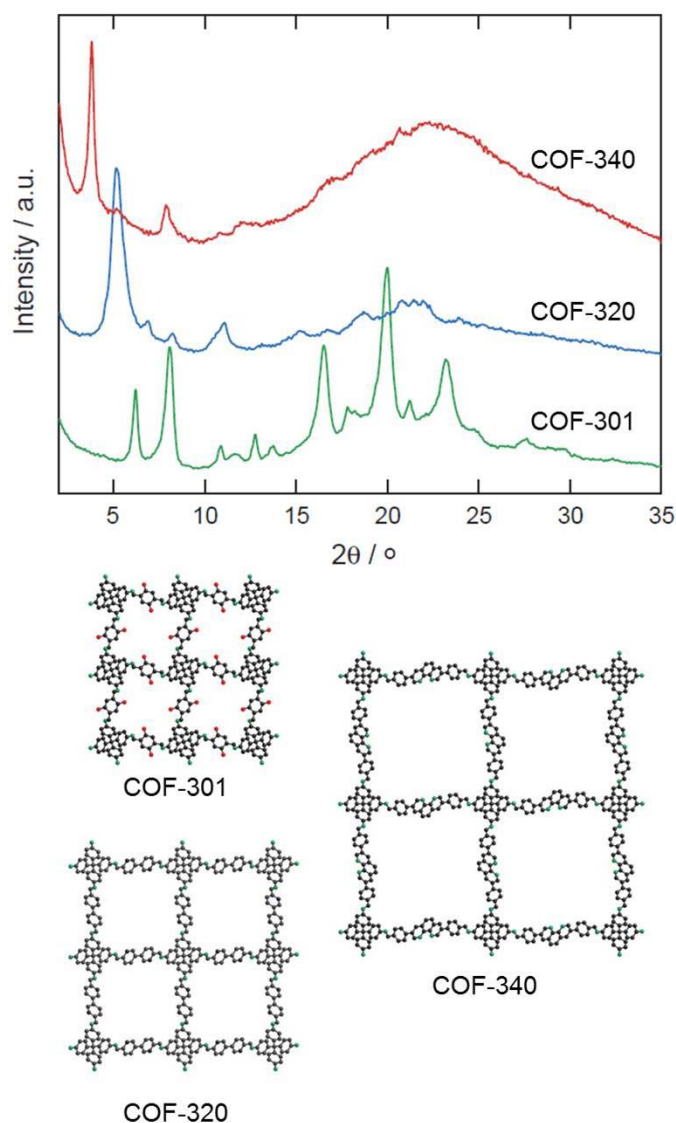
FIGURE 2. (top) PXRD patterns for COF-320 (blue) and COF-340 (red). As a reference, PXRD pattern for COF-301 was overlaid in green. (bottom) Modeled structure of COF-301, 320, and 340 based on the PXRD pattern.

weak diffraction lines observed. Further modification of the synthetic condition will be made to obtain crystalline solid.

The permanent porosity of COF-320 was demonstrated by measuring N_2 adsorption at 77 K. The application of the Brunauer-Emmett-Teller (BET) model results in a surface area of 1,620 m^2 g^{-1}, which is higher than COF-300 and 301. However, low-pressure H_2 uptake at 77 K by COF-320 was not exceptional (Figure 3). The uptake at 1 bar and 77 K was 0.6 wt%, which is smaller than COF-300 (1.1 wt%). Currently the reason is not clear why the H_2 uptake is so small; however, it is likely that the activation conditions are not optimized yet. In the case of COF-340, N_2 isotherms using activated samples were also recorded. Unexpectedly N_2 uptake was very low (BET surface area = 35 m^2 g^{-1}),
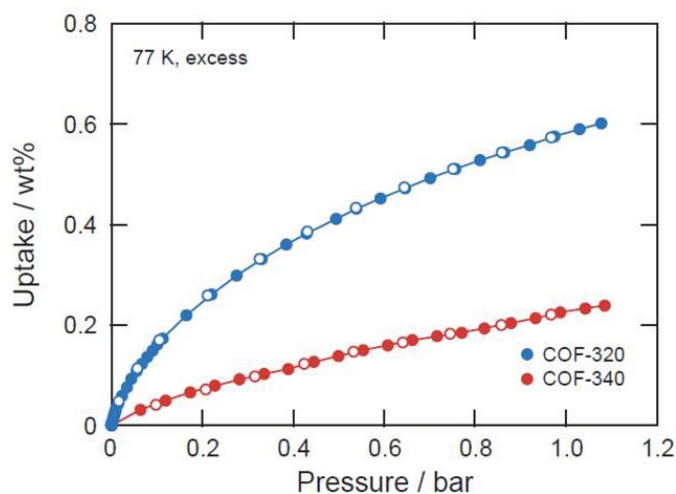

FIGURE 3. Excess H_2 isotherms of COF-320 (blue) and 340 (red) at 77 K

although the PXRD pattern indicates that the crystallinity still remains after the sample activation. Since the pore diameter of COF-340 is even greater than COF-320, this may be due to the presence of oligomers (i.e. fragments of COFs) in the pore. Currently investigation of the optimal condition to make crystalline COF-340 with reasonable porosity is now in progress.

Simulation of H_2 uptake at 298 K for COF-320, COF-322, COF-330 and COF-333. In the simulation side, the isotherms at the high pressure range for COF-320, COF-322, COF-330 and COF-333 were calculated and these are compared to the H_2 uptake of COF-300 at 298 K. It was found that the uptake for the other COFs at room temperature are very similar to each other but even higher than COF-300 (Figure 4). The maximum excess H_2 uptakes for these COFs in gravimetric units are listed in Table 1. Table 1 implies that all the compounds have a similar property. COF-320, COF-322 and COF-333 have very similar surface areas, which are greater than 7,000 m^2 g^{-1}, while COF-300 and COF-330 show lower values. This should be due to the smaller pore diameter and/or larger volume of organic linker per volume.

Next the Q_{st} value for each compound was estimated. Since all the COFs contain C, H, and N and have an imine bond, it is expected that the interaction between framework and H_2 is also similar. The degree of this interaction should be derived from the Q_{st}. Obtained initial Q_{st} values for all pristine COFs are summarized in Table 1. The values of Q_{st} are ranging from 4.3 and 5.8 kJ mol^{-1}, leading to the fact that these COFs have essentially similar binding energy of H_2. COF-300 has the lowest gravimetric uptake, while it showed the highest Q_{st} because of the small pore diameter. In this case, the potential energy surface for the pore overlaps and makes the H_2 interacts strongly with framework; however, it is well known that the small pore provides limited amount of H_2 uptake.
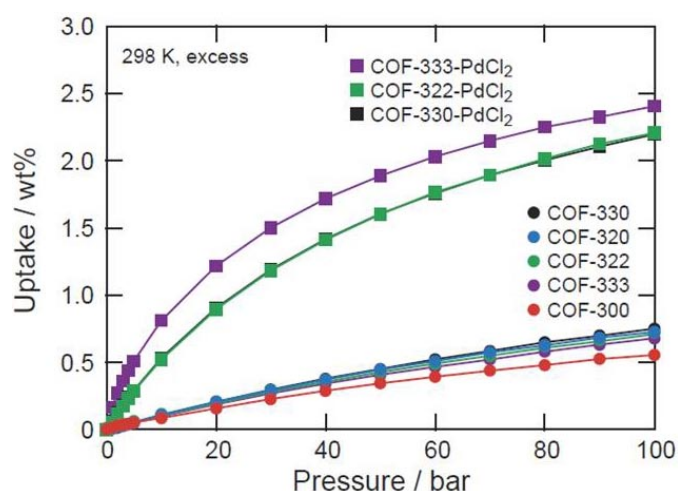
FIGURE 4. Predicted excess H_2 isotherms of COF-300, 320, 322, 330, and 333 and metalated versions of COF-322, 330, and 333 at 298 K. The values of COF-330 and COF-333 are very similar.

in Table 1. These values are higher than bulk density of H_2 (7.6 g L^{-1}) so that it is presumed that H_2 molecules are effectively trapped by metal moieties introduced in the pore.

The initial Q_{st} values for these compounds were also calculated. The Q_{st} for metalated COF-333 (19 kJ mol^{-1} and 12.4 kJ mol^{-1} in average between 1-100 bar) is higher than other materials shown in this report. Note that metalated COF-333 also demonstrates the highest total uptake in volumetric unit. COF-333 and COF-322/330 have the same topology, the same connectivity and almost the same atoms, although the density of metal binding sites is double. On the contrary, the spatial location of the metals is different; for COF-333 the metal sites are on the corners of the pore, while metal sites for COF-322/330 are in the middle of the linker. Since it is unlikely that the density of metal in the framework affects the Q_{st} value, metals sites on the corners may interact more strongly. As a result, the stronger binding energy of H_2 can show improved H_2 uptake behavior despite COF-333 having a smaller surface area.

Conclusions and Future Directions

We originally performed the metalation reactions using COF-301 and phenanthroline-COFs; however, the results implied that the pore diameter is critical to successful incorporation of the guest metal. Therefore, in the middle of this year, the synthesis of new COFs with large pores was implemented by connecting ditopic and tetratopic building units through imine condensation (COF-320 and 340). In parallel with the synthesis, the binding energy with all first row transition metals was estimated to be the best candidates. Since the results indicate these transition metals and $PdCl_2$ show greater metal-H_2 interaction, H_2 loading curves for the expanded version of COF-300 with and without $PdCl_2$ were calculated. In addition to this, two low density COFs with triptycene units (0.15-0.21 g cm^{-3}) were designed and synthesized.

Next, total and excess uptake for the metalated versions of COF-330 and COF-333 at 298 K was estimated. The excess gravimetric uptake at 298 K is shown in Figure 4. In this case, the H_2 uptake in gravimetric unit is very similar to each other; metalated COF-330 and COF-333 take up 2.2 and 2.4 wt% (excess uptake) of H_2 at 100 bar, respectively. The same trend was observed by the total uptake in gravimetric units; the uptake at 100 bar and 298 K is 3.1 and 3.2 wt% for metalated COF-330 and COF-333, respectively (Table 1).

The total volumetric uptake for these two compounds was also estimated (Table 1). It should be noted that both frameworks show much greater H_2 uptake; COF-330 has 2.5 times higher uptake at 100 bar than bulk H_2, while COF-333 has 3 times higher uptake. This clearly proves the advantage of metalation of the frameworks, although these values should be improved more. The total uptake of metalated COF-333 and 330 in volumetric unit is shown

TABLE 1. Summary of linker, and predicted surface area, H_2 uptake, and initial Q_{st} data for materials in this study

Compound	Linker	BET area (m^2 g^{-1})	Excess uptake (wt%)	Total uptake (wt%)	Total uptake (g L^{-1})	Q_{st} (kJ mol^{-1})
COF-300	1 + 2	3,820	0.55	1.4	7.9	5.8
COF-320	1 + 4	7,850	0.73	2.5	8.0	4.4
COF-322	1 + 5	7,300	0.71	2.4	8.1	4.4
COF-330	1 + 7	5,990	0.75	2.2	8.3	4.7
COF-333	1 + 6	7,710	0.68	2.4	7.9	4.3
COF-322-PdCl2	1 + 5	5,550	2.2	3.3	16	9.2
COF-330-PdCl2	1 + 7	3,930	2.2	3.1	17	9.9
COF-333-PdCl2	1 + 6	2,990	2.4	3.2	21	19

- Optimize the activation conditions for the best surface area. H_2 isotherms and Q_{st} data will be compared to the predicted data.
- Characterize metalated materials (metal binding fashion, surface area, H_2 uptake, Q_{st})
- Develop the van der Waals-Force Field for the entire row of early transition metals from our current results.
- Use 2PT approach to calculate phase diagrams for H_2 inside the pores including counter anions.
- Optimize the metalation condition and loading amount for high-pressure H_2 tests at room temperature.

Special Recognitions & Awards/Patents Issued

1. TOP 2 most cited chemist worldwide (ISI Thomson)

FY 2012 Publications

1. S. Wan, F. Gándara, A. Asano, H. Furukawa, A. Saeki, S.K. Dey, L. Liao, M.W. Ambrogio, Y.Y. Botros, X. Duan, S. Seki, J.F. Stoddart, O.M. Yaghi, "Covalent Organic Frameworks with High Charge Carrier Mobility," *Chem. Mater.* **2011**, *23*, 4094-4097.

2. F.J. Uribe-Romo, C.J. Doonan, H. Furukawa, K. Oisaki, O.M. Yaghi, "Reticular Synthesis of Mesoporous Covalent Hydrazone Frameworks," *J. Am. Chem. Soc.* **2011**, *133*, 11478-11481.

3. J.L. Mendoza-Cortes, S.S. Han, W.A. Goddard, "High H_2 Uptake in pure, Li-, Na-, K-Metalated Covalent Organic Frameworks and Metal Organic Frameworks at 298 K," *J. Phys. Chem. A* **2012**, *116*, 1621-1631.

4. J.L. Mendoza-Cortes, "Design of Molecules and Materials for Applications in Clean Energy, Catalysis and Molecular Machines through Quantum Mechanics, Molecular Dynamics and Monte Carlo Simulations," California Institute of Technology, 2012, Ph.D. thesis.

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1. H.M. El-Kaderi, J.R. Hunt, J.L. Mendoza-Cortés, A.P. Côté, R.E. Taylor, M. O'Keeffe, O.M. Yaghi, *Science*, **2007**, *316*, 268-272.

2. H. Furukawa, O.M. Yaghi, *J. Am. Chem. Soc.*, **2009**, *131*, 8876-8883.

3. J.L. Mendoza-Cortes, S.S. Han, W.A. Goddard, *J. Phys. Chem. A*, **2012**, *116*, 1621-1631.

4. F.J. Uribe-Romo, J.R. Hunt, H. Furukawa, C. Klock, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.*, **2009**, *131*, 4570.