Fiscal Year (FY) 2012 Objectives

- Design optimal frameworks with potential metal binding sites for metal impregnation.
- Predict H₂ uptake isotherm for designed frameworks using our newly developed force field.
- Implement metalation experiments and evaluate the H₂ adsorption property.
- Synthesize new covalent organic frameworks (COFs) with ultra-high surface area (>5,000 m² 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

Introduction

Storage of hydrogen in porous materials is a promising approach to achieve the DOE system requirements for use of H₂ as a transportation fuel. After the first report of successful H₂ storage in metal-organic frameworks (MOFs), the Yaghi group has succeeded in incrementally increasing the gravimetric and volumetric capacities in order to reach the highest H₂ uptake capacity, albeit at 77 K. However, for onboard vehicular H₂ 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 H₂.

Approach

To meet the DOE 2015 revised 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 previously demonstrated how to design high surface area MOFs and COFs [1]. However, in many cases, these materials do not show steep H₂ 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 versions 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 tetrapoic (1) and ditopic building units (2-8), which form COF materials. The name of each COF is shown in parentheses.](image-url)

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
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\textsubscript{2} adsorption at 77 K. The application of the Brunauer-Emmett-Teller (BET) model results in a surface area of 1,620 m\textsuperscript{2} g\textsuperscript{-1}, which is higher than COF-300 and 301. However, low-pressure H\textsubscript{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\textsubscript{2} uptake is so small; however, it is likely that the activation conditions are not optimized yet. In the case of COF-340, N\textsubscript{2} isotherms using activated samples were also recorded. Unexpectedly N\textsubscript{2} uptake was very low (BET surface area = 35 m\textsuperscript{2} g\textsuperscript{-1}), 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\textsubscript{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\textsubscript{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\textsubscript{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\textsuperscript{2} g\textsuperscript{-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 \textit{Q}_s 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\textsubscript{2} is also similar. The degree of this interaction should be derived from the \textit{Q}_s. Obtained initial \textit{Q}_s values for all pristine COFs are summarized in Table 1. The values of \textit{Q}_s are ranging from 4.3 and 5.8 kJ mol\textsuperscript{-1}, leading to the fact that these COFs have essentially similar binding energy of H\textsubscript{2}. COF-300 has the lowest gravimetric uptake, while it showed the highest \textit{Q}_s, because of the small pore diameter. In this case, the potential energy surface for the pore overlaps and makes the H\textsubscript{2} interacts strongly with framework; however, it is well known that the small pore provides limited amount of H\textsubscript{2} uptake.
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 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 $Q_m$ values for these compounds were also calculated. The $Q_m$ 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 $Q_m$ 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.

**TABLE 1.** Summary of linker, and predicted surface area, $H_2$ uptake, and initial $Q_m$ data for materials in this study

<table>
<thead>
<tr>
<th>Compound</th>
<th>Linker</th>
<th>BET area (m$^2$ g$^{-1}$)</th>
<th>Excess uptake (wt%)</th>
<th>Total uptake (wt%)</th>
<th>Total uptake (g L$^{-1}$)</th>
<th>$Q_m$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>COF-300</td>
<td>1 + 2</td>
<td>3,820</td>
<td>0.55</td>
<td>1.4</td>
<td>7.9</td>
<td>5.8</td>
</tr>
<tr>
<td>COF-320</td>
<td>1 + 4</td>
<td>7,850</td>
<td>0.73</td>
<td>2.5</td>
<td>8.0</td>
<td>4.4</td>
</tr>
<tr>
<td>COF-322</td>
<td>1 + 5</td>
<td>7,300</td>
<td>0.71</td>
<td>2.4</td>
<td>8.1</td>
<td>4.4</td>
</tr>
<tr>
<td>COF-330</td>
<td>1 + 7</td>
<td>5,990</td>
<td>0.75</td>
<td>2.2</td>
<td>8.3</td>
<td>4.7</td>
</tr>
<tr>
<td>COF-333</td>
<td>1 + 6</td>
<td>7,710</td>
<td>0.68</td>
<td>2.4</td>
<td>7.9</td>
<td>4.3</td>
</tr>
<tr>
<td>COF-322-PdCl$_2$</td>
<td>1 + 5</td>
<td>5,550</td>
<td>2.2</td>
<td>3.3</td>
<td>16</td>
<td>9.2</td>
</tr>
<tr>
<td>COF-330-PdCl$_2$</td>
<td>1 + 7</td>
<td>3,930</td>
<td>2.2</td>
<td>3.1</td>
<td>17</td>
<td>9.9</td>
</tr>
<tr>
<td>COF-333-PdCl$_2$</td>
<td>1 + 6</td>
<td>2,990</td>
<td>2.4</td>
<td>3.2</td>
<td>21</td>
<td>19</td>
</tr>
</tbody>
</table>
• Optimize the activation conditions for the best surface area. H₂ isotherms and $Q_{st}$ data will be compared to the predicted data.
• Characterize metalated materials (metal binding fashion, surface area, H₂ 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 H₂ inside the pores including counter anions.
• Optimize the metalation condition and loading amount for high-pressure H₂ tests at room temperature.

**Special Recognitions & Awards/Patents Issued**

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

**FY 2012 Publications**


**References**