

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

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Contract Number: DE-FG36-08GO18141

Project Start Date: September 1, 2008 (funded from April 1, 2009)

Project End Date: January 31, 2013

Technical Targets

This project consists of several fundamental studies on COFs and ZIFs. 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 2011 Accomplishments

- Synthesized new COFs via hydrazone and imine condensation.
- Initiated metalation experiments of COFs.
- Began synthesis of mixed-metal ZIFs for improved adsorption enthalpy.
- Found linkers with optimal binding energy for H₂ storage (20 kJ/mol).
- Designed new architectures with these linkers and began simulation calculations of H₂ uptake.

Fiscal Year (FY) 2011 Objectives

- Design new covalent-organic frameworks (COFs) with strong H₂ binding sites.
- Predict H₂ uptake isotherm for designed frameworks employing a developed force field.
- Prepare stable frameworks with potential metal binding sites.
- Implement metalation experiments and evaluate their respective H₂ adsorption properties.
- Prepare a mixed-metal zeolitic imidazolate framework (ZIF).

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 on-board 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; however, in many cases, these materials do not show steep H₂ uptake in the low-pressure region indicative of the weak interaction with H₂. It is predicted that the impregnation of COFs with metals will enhance the

adsorption enthalpy, which has led us to explore methods for the preparation of metalated COFs. In this FY, we developed a new class of COFs for metal impregnation. Moreover, we developed the force field from *ab initio* calculations, which are used to estimate the isotherm of COFs containing the hydrazone and imine moieties as well as the H₂ uptake for a full and partial Pd(II)-metalated COFs. In addition, a new mixed-metal ZIF was designed and synthesized to incorporate strong H₂ binding sites in the framework.

Results

Metal impregnation is one of the most promising strategies to improve the adsorption enthalpy of COFs. However, before the metal impregnation experiments are carried out, it is necessary to prepare stable COFs that are capable of introducing metal binding sites in the framework through the condensation reaction. To this end, we designed and prepared new COFs having hydrazone and imine moieties.

Preparation of Hydrazone COF. Despite the significant interest in developing COFs for industrially relevant applications, only a small number of organic functionalities, such as boronates, borosilicate, and imine condensations have been employed in their preparation [1-3]. The relatively few examples of COF architectures, with respect to the vast library of possible organic reactions, can be attributed to the significant challenge of synthesizing crystalline solids constructed solely from strong covalent bonds. We have previously shown that this challenge is overcome by using dynamic covalent systems coupled with precisely controlled reaction conditions. Thus, we employed these same principles in the selection of hydrazide and aldehyde moieties as novel building blocks for COF

materials since the reversibility of hydrazone formation by modulating the pH is well documented.

COF-42 and COF-43 were synthesized by suspending 2,5-diethoxyterephthalohydrazide (1) and 1,3,5-triformylbenzene (2) or 1,3,5-tris(4-formylphenyl)benzene (3) in a flame-sealed Pyrex tube in a mixture of mesitylene, dioxane and acetic acid at 120°C (Figure 1). These materials were immersed in tetrahydrofuran to remove occluded guests for three days, and the solvent was subsequently removed by heating at 85°C under dynamic vacuum.

Powder X-ray diffraction (PXRD) measurements were performed on samples of COF-42 and COF-43 to determine their crystallinity. The experimental PXRD patterns of both COFs were indexed based on a primitive hexagonal lattice. Next, the raw data was compared to models of possible crystal structures that can be obtained from linking the trigonal and the linear building blocks. It is anticipated that two-dimensional trigonal layers will be formed given that the hydrazone moiety is approximately coplanar with respect to the aromatic rings due to resonance effects and internal hydrogen bonding. These layers can pack in eclipsed **bnn** (*P6/mmm*), or staggered modes, **gra** (*P6₃/mmc*). However, at this resolution, the framework topologies, for both COFs, as either **bnn** or **gra** could not be assigned.

Gas adsorption isotherms were measured on fully activated samples in order to ensure the architectural stability and porosity of each COF. The Ar isotherm of COF-42 measured at 87 K showed a sharp uptake below $P/P_0 = 0.05$ with a step at $P/P_0 = 0.05-0.20$. This profile is best described as Type IV isotherm, which is characteristic of mesoporous materials. The Brunauer-Emmett-Teller (BET) surface area of COF-42 was calculated to be 710 m² g⁻¹. The 87 K Ar adsorption isotherm of COF-43 also possesses a type IV shape indicating that it is a mesoporous material. The BET surface area of COF-43 was calculated

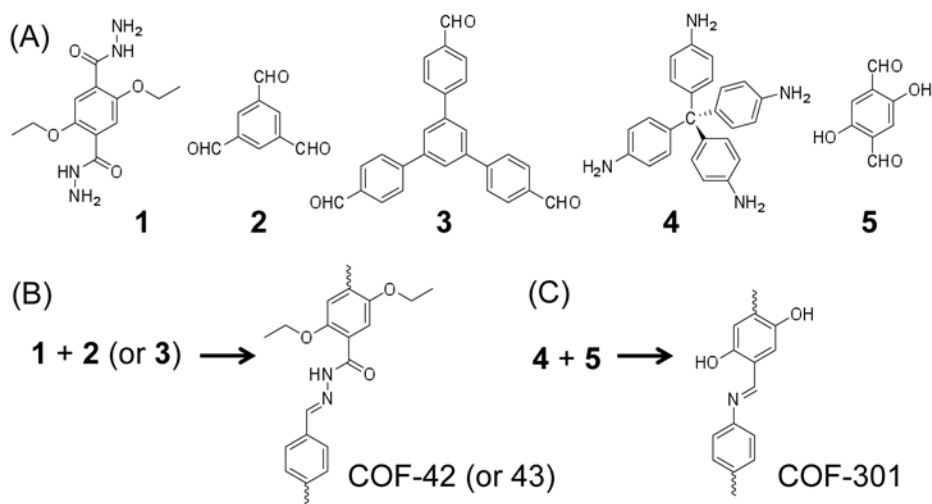


FIGURE 1. (A) Molecular structures of building units for COF synthesis. Reaction scheme of hydrazone (B) and imine COF (C) formation.

to be $620 \text{ m}^2 \text{ g}^{-1}$. Notably, the surface area and pore volume values obtained for COF-42 and COF-43 are comparable to those of other two-dimensional COFs with hexagonal pore systems [4]. A non-local density functional theory model was fitted to the isotherms of COF-42 and COF-43 yielding average pore sizes of 23 and 38 Å, respectively, these values are in good agreement with the expected pore size observed in the crystal simulations based on a **bnn** topology. More importantly, this is large enough to accommodate metal ions (and possibly their counter anions) in the pore.

The H_2 isotherms for these COFs are illustrated in Figure 2. The H_2 uptake for COF-42 and 43 at 1 bar and 77 K is 0.60 and 0.51 wt%, respectively. Although COF-42 has a smaller BET surface area, the H_2 uptake for COF-42 under the present experimental conditions was larger than that of COF-43. We attribute these results to the smaller pore diameter of COF-42. Furthermore, this theory is supported by the isosteric heats of adsorption (Q_{st}) data for these COFs (Figure 2, inset). The initial Q_{st} values for both COFs are almost the same (6.6 kJ/mol), because of the similarity in the surface environment of COFs. Once a majority of strong binding sites are occupied by H_2 , the adsorption potential in the pore should be more important (i.e. larger pore material has smaller adsorption potential). Consequently, it is likely that the values for COF-43 quickly dropped with an increase in the H_2 loading.

Preparation of Imine COF and its Metalation

Reaction. We have demonstrated the condensation of the tetrahedral building block tetra-(4-anilyl)methane with the linear linking unit terephthalaldehyde to produce a material with an extended three-dimensional framework structure (COF-300) [3]. COF-300 is an interpenetrated diamond net and has a one-dimensional channel with diameter of 7.8 Å. However, due to the lack of potential metal binding sites, it is not easy to metalate this material. To create

metal binding sites in the COF frameworks, we believe salicylidene-aminophenyl and iminopyridine moieties are good candidates. This year, we synthesized a new imine COF (termed COF-301).

The synthesis of COF-301 was carried out by solvothermal synthesis of a suspension of tetra-(4-anilyl)methane (4) and 2,5-dihydroxyterephthalaldehyde (5) in a mixture of 1,4-dioxane and aqueous acetic acid (Figure 1). The material is insoluble in water and common organic solvents such as hexanes, methanol, acetone, tetrahydrofuran, and *N,N*-dimethylformamide. Therefore, it seems the resultant crystalline material is an extended structure. The formation of imine linkages in COF-301 was confirmed by Fourier transform infrared spectra. The crystallinity of COF-301 was confirmed by PXRD analysis. Although its atomistic connectivity is not determined yet, it is presumed that the connectivity (topology) of COF-301 is a diamond net due to the similarity of PXRD pattern. However, no information is available with regard to the degree of interpenetration.

The permanent porosity of COF-301 was demonstrated by measuring N_2 adsorption at 77 K. The isotherm shows a sharp uptake below $P/P_0 < 0.10$. The application of the BET model results in a surface area of $1,040 \text{ m}^2/\text{g}$. The N_2 isotherm was fit with non-local density functional theory models from which the pore size distribution was calculated, resulting in a value of 10.5 Å, which is close to the values observed in the proposed structure (ca. 9.5 Å).

Prior to the metalation reaction, we predicted the total H_2 isotherms of pristine and COF-301-Pd (using PdCl_2 as the source) with different metal loadings. As shown in Figure 3, metalated material shows steep H_2 uptake below 10 bar even at room temperature, which is in sharp contrast to the pristine COF-301. The total H_2 uptakes at 100 bar are calculated to be 4.5, 3.7, 2.7 wt% for 100%, 50%, and 25%

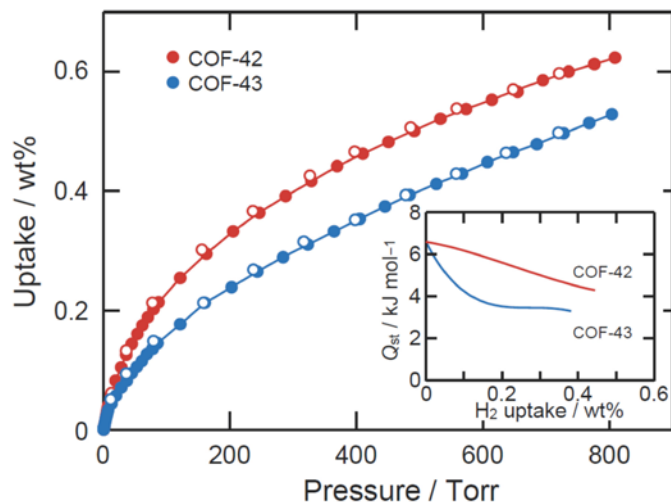


FIGURE 2. H_2 isotherms for COF-42 (red) and COF-43 (blue) at 77 K. Inset: coverage dependence of the isosteric heats of adsorption (Q_{st}) for H_2 in these COFs.

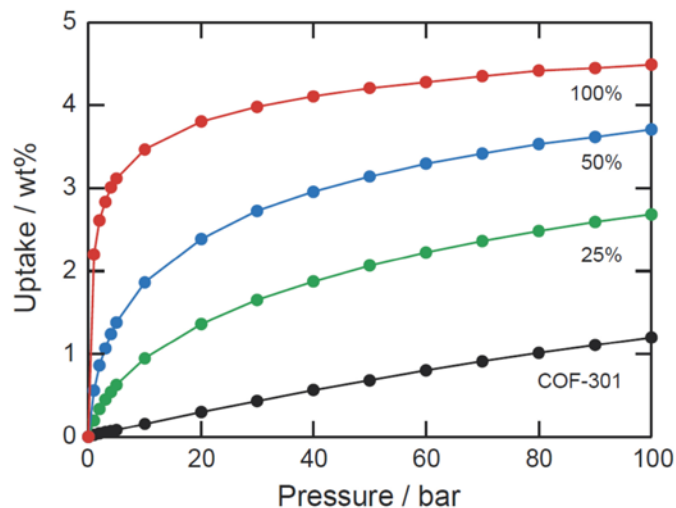


FIGURE 3. Predicted total gravimetric H_2 isotherms of pristine COF-301 and COF-301- PdCl_2 with different metal loadings (100%, 50%, and 25%).

Pd loading COF-301. These values are much greater than pristine COF-301 (1.2 wt%) under the same condition, so that it is presumed that the interaction between Pd and H₂ is strong enough to improve the H₂ uptake capacity. This is more obvious when we observe the average Q_{st} values which are 23.6, 17.8, 14.0 kJ/mol for 100%, 50%, and 25% Pd loading COF-301, while only 6.0 kJ/mol for pristine COF-301. Although the metalated compound would have a smaller pore volume and a larger bulk density, the simulated isotherms encourage us to implement the metalation. Therefore, we impregnated COF-301 with metal salts, and obtained materials are termed COF-301-M; M = Pd(II) and Pt(II).

The metalation of COF-301 was carried out by reflux reaction of a suspension of COF-301 and metal source (PdCl₂ or PtCl₂) in acetonitrile. The resulting yellow solid was filtered off, washed with ethanol, diethyl ether and dried under vacuum. After the metalation, the peak position of PXRD for metalated COF-301 is almost identical to that of COF-301. Therefore, we believe that the crystallinity of these metalated materials is retained, although the intensity of the pattern decreased. Currently, we do not have clear evidence to confirm whether the metal ion was bound to the framework. We plan to study the metal coordination environment using ¹⁵N enriched material.

Before the H₂ tests, we measured N₂ isotherms of a series of materials. After the metalation, the BET surface areas of the samples were much smaller than that of the pristine material (60 m²/g for COF-301-Pd, 20 m²/g for COF-301-Pt). Although the metalated samples have a larger density than the original COF-301, this should not be the only reason for the significant surface area drop. Possible explanation of this drop is (i) the presence of leaving groups (perhaps two Cl) bound to the metal ion and/or unreacted metal salts (i.e. MCl₂), (ii) pore openings of the metalated samples could be partly blocked, which would reduce the accessible pore space, and/or (iii) crystallinity of the materials were partially lost. To mitigate the surface area drop, we will optimize metalation and sample activation conditions.

Preparation of Mixed-Metal ZIFs. To improve H₂ storage capacity, the number of metals per volume is a very important factor to keep in mind. In most cases, ZIFs have higher metal density because the length of the imidazolate is short [5]. However, these metal ions (i.e. Zn²⁺ and Co²⁺) are fully coordinated to imidazolate linkers such that it is difficult to utilize these metals as strong H₂ binding sites. We believe it is possible to create open metal sites in ZIF structures, if we introduce another metal ion having different coordination geometry. To this end, we added another metal source (Cu²⁺) to reaction mixtures.

The as-synthesized product (ZnCu(imidazolate)) was washed with methanol and evacuated at room temperature. The permanent porosity of the activated sample was confirmed by N₂ adsorption at 77 K. The profile of the N₂ isotherm for evacuated samples is classified typical Type I isotherm, whose BET surface area is calculated to

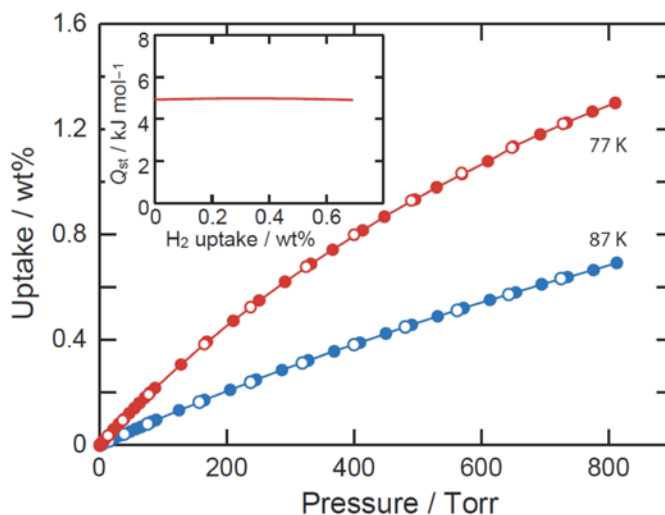


FIGURE 4. H₂ isotherms for the mixed metal ZIF at 77 K (red) and 87 K (blue). (Inset) Coverage dependence of the isosteric heat of adsorption (Q_{st}) for H₂ in the ZIF calculated from fits of its 77 and 87 K isotherms.

be 1,460 m²/g. This is one of the highest values in ZIF materials, although these are slightly smaller than ZIF-8 [6]. The H₂ isotherms for mixed metal ZIF are illustrated in Figure 4. The H₂ uptake at 1 bar and 77 K is 1.2 wt%. Considering that the isotherm is nearly straight in this region, the interaction between the framework and H₂ may not be strong. Indeed, the Q_{st} value did not change until 0.7 wt% of H₂ coverage (Figure 4, inset). Currently, we are studying the synthetic conditions for other mixed metal ZIFs with different metal ions with square planar geometry (e.g. Ni).

Conclusions and Future Directions

This year we experimentally demonstrated how to introduce potential metal binding moieties by connecting di-, tri-, and tetra-topic building units through condensation reactions (i.e. hydrazine and imine COFs). We started the metalation reactions using COF-301, although the metalation conditions are not optimized yet. We plan to screen candidates for metalation reactions of COFs through modeling studies, which will be experimentally evaluated. In addition, we will predict the binding energy between H₂ and metal unit.

- Material design assisted by the reticular synthesis.
- Calculate the H₂ isotherms for pristine and metalated COFs.
- Implement the metalation reaction based on the theoretical prediction.
- Calculate the free energy (ΔG) and enthalpy (ΔH) for the metalation processes.
- Calculate the diffusion coefficient of H₂ in the frameworks to estimate the kinetic factor.

- Synthesize mixed metal ZIFs with different metal ions.
- Begin calculation of H₂ isotherms for mixed metals ZIFs.

Special Recognitions

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

FY 2011 Publications

1. S.S. Han, S.H. Choi, W.A. Goddard, "Zeolitic Imidazolate Frameworks as H₂ Adsorbents: Ab Initio Based Grand Canonical Monte Carlo Simulation," *J. Phys. Chem. C*, **2010**, *114*, 12039-12047.
2. 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.*, accepted.
3. 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.
4. J.L. Mendoza-Cortes, S.S. Han, W.A. Goddard, "High H₂ Uptake in pure, Li-, Na-, K-metalated Covalent Organic Frameworks and Metal Organic Frameworks at 298 K," submitted.

5. F.J. Uribe-Romo, "Design, synthesis and powder diffraction crystallography of porous framework materials", University of California - Los Angeles, 2010, Ph. D. thesis.

References

1. A.P. Côté, A.I. Benin, N.W. Ockwig, M. O'Keeffe, A.J. Matzger, O.M. Yaghi, *Science*, **2005**, *310*, 1166.
2. J.R. Hunt, C.J. Doonan, J.D. LeVangie, A.P. Côté, O.M. Yaghi, *J. Am. Chem. Soc.*, **2008**, *130*, 11872.
3. F.J. Uribe-Romo, J.R. Hunt, H. Furukawa, C. Klock, M. O'Keeffe, O.M. Yaghi, *J. Am. Chem. Soc.*, **2009**, *131*, 4570.
4. A.P. Côté, H.M. El-Kaderi, H. Furukawa, J.R. Hunt, O.M. Yaghi, *J. Am. Chem. Soc.*, **2007**, *129*, 12914.
5. A. Phan, C.J. Doonan, F.J. Uribe-Romo, C.B. Knobler, M. O'Keeffe, O.M. Yaghi, *Acc. Chem. Res.*, **2009**, *43*, 58.
6. K.S. Park, Z. Ni, A.P. Côté, J.Y. Choi, R.D. Huang, F.J. Uribe-Romo, H.K. Chae, M. O'Keeffe, O.M. Yaghi, *Proc. Natl. Acad. Sci. U.S.A.*, **2006**, *103*, 10186.