

## IV.C.10 Metal- and Cluster-Modified Ultrahigh-Area Materials for the Ambient Temperature Storage of Molecular Hydrogen

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Project Start Date: November 1, 2011

Project End Date: Project continuation and direction determined annually by DOE

### Fiscal Year (FY) 2012 Objectives

- Synthesis of –OH and –NH<sub>2</sub> functionalized ultrahigh-area sorbents
- Develop strategies to introduce metal cations into ultrahigh-area sorbents
- Evaluate materials performance of metal functionalized ultrahigh-area sorbents

### Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) System Weight and Volume
- (E) Charging/Discharging Rates
- (P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

### Technical Targets

This project consists of developing ultrahigh-area sorbents capable of being modified with divalent metal cations. These materials aim to meet the DOE 2017 hydrogen storage targets:

- System Gravimetric Capacity: 1.8 kWh/kg (0.055 kg H<sub>2</sub>/kg system)
- System Volumetric Capacity: 1.3 kWh/L (0.040 kg H<sub>2</sub>/L system)

### FY 2012 Accomplishments

- Synthesis of ultrahigh-area sorbents and –OH and –NH<sub>2</sub> functionalized sorbents
- Atomic layer deposition (ALD) and solution-based metallation of –OH and –NH<sub>2</sub> functionalized sorbents
- Initial materials performance analysis for increased  $Q_{st}$



### Introduction

Ultrahigh-area physisorption-based sorbents—for example, metal-organic frameworks (MOFs) and porous organic polymers (POPs)—are attractive candidates for the storage of molecular hydrogen (H<sub>2</sub>). MOFs and POPs are built up from well-defined molecular components and key material properties such as pore size and functionality can often be readily controlled. On a materials basis, some of these sorbents meet the DOE's technical targets for both gravimetric and volumetric capacity, albeit at cryogenic temperatures. A crucial challenge for physisorption-based sorbents has therefore been storage of H<sub>2</sub> at or near room temperature. Storing H<sub>2</sub> at or near room temperature will require sorbents that can bind H<sub>2</sub> more effectively.

### Approach

Our approach relies on introducing coordinatively unsaturated metal cation sites into (–OH or –NH<sub>2</sub>) functionalized ultrahigh-area (i.e., ≥3,000 m<sup>2</sup>/g) physisorption-based sorbents. Recent computational evidence has suggested that divalent metal cations are capable of achieving the binding energies (isosteric heat of adsorption ( $Q_{st}$ ) ~20–30 kJ/mol) necessary to store H<sub>2</sub> at room temperature [1]. We are pursuing three metallation strategies: (i) introduction of divalent metal cations via ALD; (ii) introduction of small metal-oxo(hydroxy) clusters via ALD;

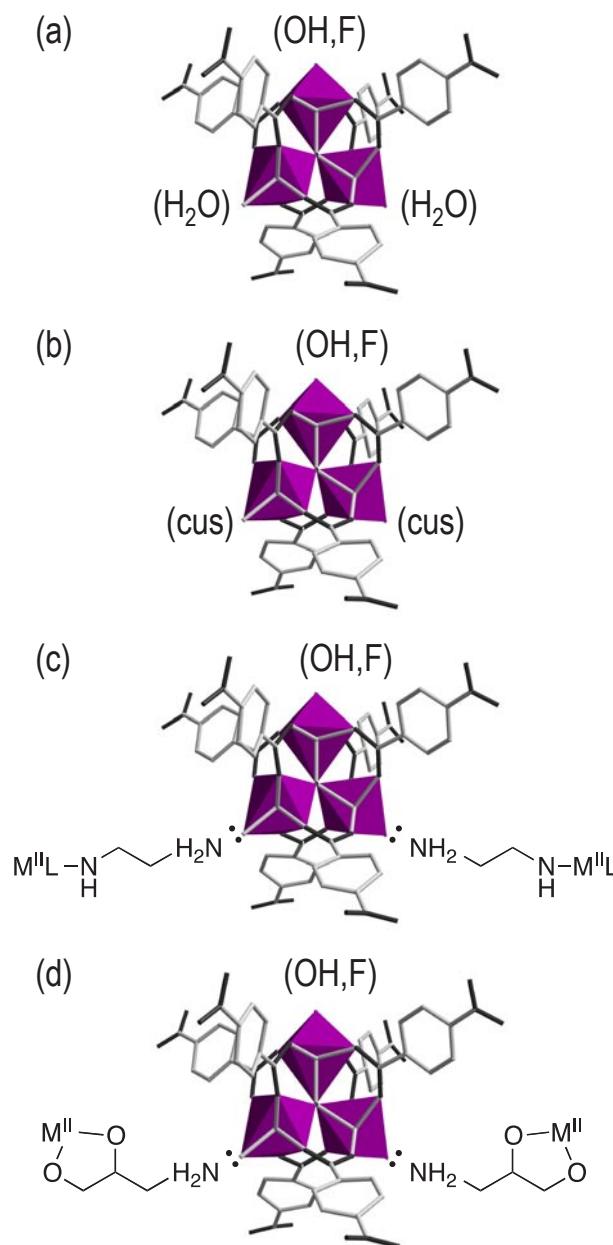
and (iii) introduction of divalent metal cations via precedent solution chemistry [2].

ALD is an intriguing vapor phase deposition technique that, at least in principle, is capable of depositing divalent metal ions and small metal-oxo(hydroxy) clusters on ultrahigh aspect ratio structures such as MOFs and POPs. The unique feature of ALD is that it relies on self-limiting chemical surface reactions, allowing precise, atomic level control over both the location and number of metal (and -oxo(hydroxy)) species deposited. This in turn will allow precise tuning of the  $H_2$  binding energies within metallated MOF or POP sorbents.

## Results

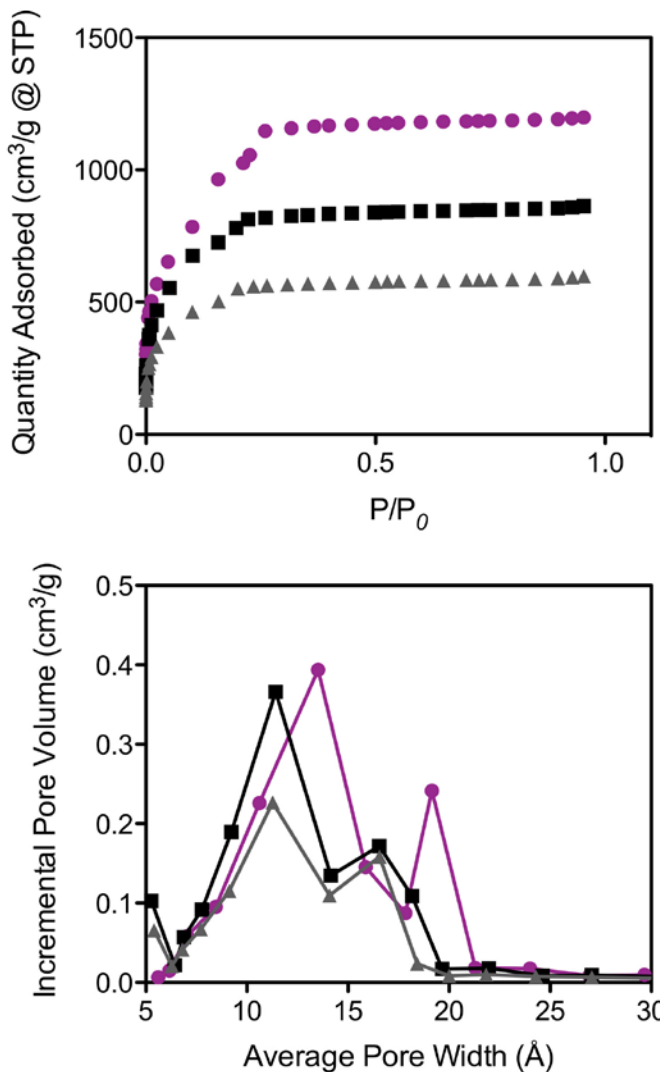
As an ultrahigh-area platform, we synthesized the well-known MOF, MIL-101; shown in Figure 1a is the  $[Cr_3(F,OH)(H_2O)_2O(bdc)_3]$  building block that MIL-101 is built up from [3]. MIL-101 is thermally stable ( $\sim 275^\circ C$ ), has ultrahigh surface areas ( $\sim 4,000 \text{ m}^2/\text{g}$ ) and large pores (29 and 34 Å)—attributes which are desirable for metal modification. Functionality was introduced into MIL-101 post-synthetically. Dehydration of MIL-101 exposed coordinatively unsaturated  $Cr^{III}$  centers and subsequent addition of ethylenediamine (ED) or 3-aminopropane-1,2-diol (APD) from solution yields MIL-101 derivatives with  $-NH_2$  or  $-OH$  functionality respectively. As expected, the surface area for both ED-MIL-101 and APD-MIL-101 decrease with respect to MIL-101, while still remaining porous (Figure 2). The decreasing Barrett, Joyner and Halenda pore-size-distributions (Figure 2) are also consistent with the  $-NH_2$  moieties of ED and APD binding to cus  $Cr^{III}$  centers in MIL-101 [3].

Subsequently ED-MIL-101 and APD-MIL-101 were subject to treatment with  $Zn(Et)_2$  in an ALD reactor. Zn metallation was quantified by inductively coupled plasma-optical emission spectroscopy, the Zn:Cr ratios were slightly higher than expected, a result which is most likely due to the ALD process scavenging any unreacted hydroxyl sources present within ED-MIL-101 and APD-MIL-101 (e.g., bdc,  $H_2O$ , etc...).  $H_2$  isotherms were measured at 77 and 87 K and the  $Q_{st}$  were extracted using a virial analysis. Figure 3 depicts the  $Q_{st}$  at constant  $H_2$  coverage for APD-MIL-101 and Zn-modified APD-MIL-101. A slight increase in  $Q_{st}$  was observed at zero  $H_2$  coverage for the Zn-modified material vs. the parent, APD-MIL-101 (note that the error bars in the measurement are smaller than the plotted data points). The results suggest that ALD may be an effective synthetic strategy to incorporate divalent metals into MOFs and therefore lead to increased  $Q_{st}$  if more favorable synthetic conditions can be found. In particular, the Zn metallated APD-MIL-101 lost much of its surface area ( $\sim 75\%$ ) and was not crystalline (Figure 3).



**FIGURE 1.** Representations of (a) MIL-101, (b) dehydrated MIL-101, (c) post-synthesis metallated ED-MIL-101 and (d) post-synthesis metallated APD-MIL-101. Coordinatively unsaturated  $Cr^{III}$  sites are represented by cus, while divalent metal cations are represented as  $M^{II}$ .

We also metallated APD-MIL-101 with  $Mg(CH_3)_2$  from a dry,  $O_2$ -free solution of toluene. The 77 and 87 K  $H_2$  isotherms were collected and the  $Q_{st}$  are plotted in Figure 3. Again we observed a slight increase in the  $Q_{st}$ , with a large loss in surface area ( $\sim 75\%$ ) and loss of crystallinity in the X-ray diffraction.

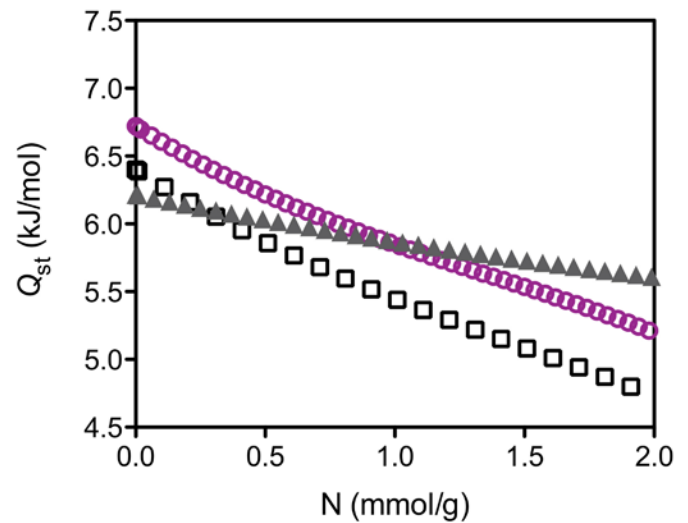


**FIGURE 2.**  $N_2$  gas adsorption isotherms (top) and Barrett, Joyner and Halenda pore size distributions (bottom) for MIL-101 (purple circles), ED-MIL-101 (black squares) and APD-MIL-101 (gray triangles)

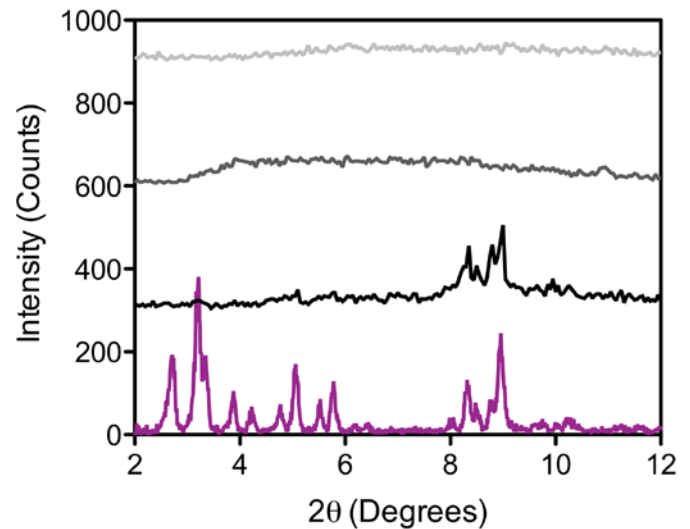
## Conclusions and Future Directions

### Conclusions

- $-NH_2$  and  $-OH$  functionalized sorbents with surface areas of  $\sim 2,000$ - $2,800$   $m^2/g$  have been synthesized and characterized
- Divalent metals (Zn and/or Mg) have been incorporated into ED-MIL-101 and APD-MIL-101
- $Q_{st}$  heats of adsorption have been obtained for all metalated (and parent) materials



**FIGURE 3.**  $Q_{st}$  at constant  $H_2$  coverage for APD-MIL-101 (gray triangles), Zn-APD-MIL-101 (purple circles) and Mg-APD-MIL-101 (black squares)



**FIGURE 4.** Powder X-ray diffraction patterns for MIL-101, APD-MIL-101, Zn-APD-MIL-101 and Mg-APD-MIL-101 (from bottom to top)

### Future Directions

- Find synthetic conditions which retain the MOF crystallinity and surface area after post-synthesis metallation
- Build small metal-oxo(hydroxy) clusters in ED-MIL-101 and APD-MIL-101 via ALD
- Experimentally screen additional metals for enhanced  $Q_{st}$
- Synthesis of  $-NH_2$  and  $-OH$  functionalized POPs and subsequent metallation

## Special Recognitions & Awards/Patents Issued

1. DOE EERE postdoctoral research awardee.

## FY 2012 Publications/Presentations

1. Mondloch, J.E.; Farha, O.K.; Hupp, J.T. "Metal- and Cluster-Modified Ultrahigh-Area Diamond Network Materials for the Ambient Temperature Storage of Molecular Hydrogen" Presented at Annual DOE EERE Postdoctoral Research Meeting, Washington, D.C., 2012.

## References

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2. Mulfort, K.L.; Farha, O.K.; Stern, C.L.; Sarjeant, A.A.; Hupp, J.T. *J. Am. Chem. Soc.* "Post-Synthesis Alkoxide Formation within Metal-Organic Framework Materials: A Strategy for Incorporating Highly Coordinatively Unsaturated Metal Ions" *J. Am. Chem. Soc.* **2009**, *131*, 3866.
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