

IV.C.5 Metallation of Metal–Organic Frameworks: En Route to Ambient Temperature Storage of Molecular Hydrogen

Joseph E. Mondloch (Primary Contact),
Joseph T. Hupp, Omar K. Farha
Northwestern University
2145 Sheridan Road
Evanston, IL 60208
Phone: (847) 467-4932
Email: mojo0001@gmail.com

DOE Managers

Channing Ahn
Phone: (202) 586-9490
Email: Channing.Ahn@ee.doe.gov
Ned Stetson
Phone: (202) 586-9995
Email: Ned.Stetson@ee.doe.gov

Technical Advisor

Joseph T. Hupp
Phone: (847) 491-3504
Email: j-hupp@northwestern.edu

Contract Number: AC05-06OR23100.

Project Start Date: November 1, 2011
Project End Date: November 1, 2013

Technologies Office Multi-Year Research, Development and Demonstration Plan:

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

Technical Targets

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

- System Gravimetric Capacity:
 - 1.8 kWh/kg (0.055 kg H₂/kg system)
- System Volumetric Capacity:
 - 1.3 kWh/L (0.040 kg H₂/L system)

FY 2013 Accomplishments

- Synthesis of a robust and functionalized high-area sorbent platform for metallation
- Solution and vapor-phase (atomic layer deposition, ALD) metallation of functionalized high-area sorbents
- Materials performance analysis (quantify Q_{st})



Overall Objectives

- Synthesis of robust –OH or –NH₂ functionalized sorbents
- Develop synthetic strategies to incorporate metal cations and clusters into functionalized sorbents
- Materials characterization and performance for room temperature physisorption-based storage (isosteric heat of adsorption [Q_{st}] between 15 and 25 kJ/mol)

Fiscal Year (FY) 2013 Objectives

- Synthesis of –OH functionalized sorbent platform for routine metallation
- Solution and vapor-phase metallation of –OH functionalized sorbents
- Materials characterization and performance analysis

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell

INTRODUCTION

Physisorption-based sorbents such as metal-organic frameworks (MOFs) are attractive candidates for the storage of molecular hydrogen (H₂). MOFs are built up from well-defined molecular components and key functional material properties, such as pore size and functionality, can 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 H₂ at or near room temperature. Storing H₂ at or near room temperature will require sorbents that can bind H₂ more effectively.

APPROACH

Our approach relies on introducing coordinatively unsaturated metal cation sites into (–OH or –NH₂)

functionalized high-area physisorption-based MOFs. Recent computational evidence has suggested that divalent metal cations are capable of achieving the binding energies (Q_{st} ~15-25 kJ/mol) necessary to store H_2 at room temperature [1]. Most often coordinatively unsaturated metal sites are introduced from the condensed phase (i.e., from solution). While we are pursuing solution-based metallation as well, our focus has shifted towards utilizing a vapor-phase metallation technique—ALD.

ALD is capable of depositing mono-, di-, tri- and tetra-valent metal cations, as well as small metal-oxo(hydroxy) clusters, into ultra-high aspect ratio structures such as MOFs [2]. 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 sorbents. Furthermore, because deposition occurs in the vapor-phase, we avoid purification and activation steps and circumvent problems associated with (H_2 sorption) site blocking solvent molecules [3].

RESULTS

We employed a new synthetic strategy capable of metallating MOFs from the vapor-phase: ALD. The key to enabling metallation by ALD in MOFs (AIM) was the synthesis of a new MOF, NU-1000 (Figure 1). NU-1000 is a Zr-based MOF that is thermally and hydrothermally stable (~500°C) and contains large one-dimensional mesopores and apertures (required for diffusion of vapor-phase precursors). The structure is built up from $Zr_6(\mu_3-OH)_8(-OH)_8$ nodes and

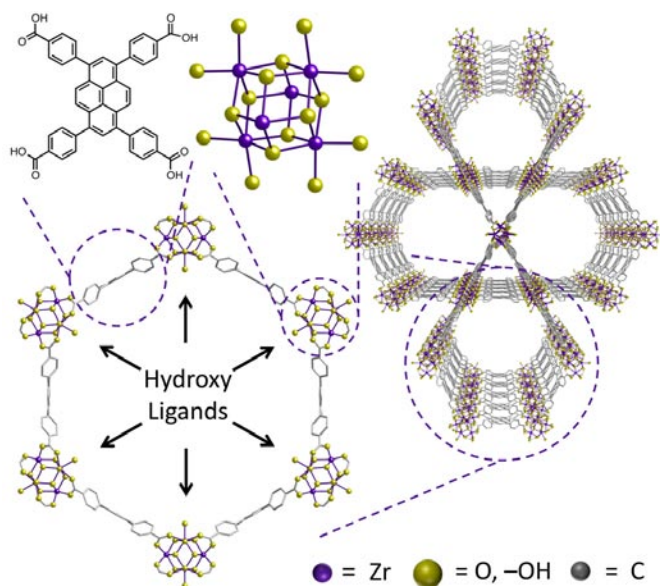
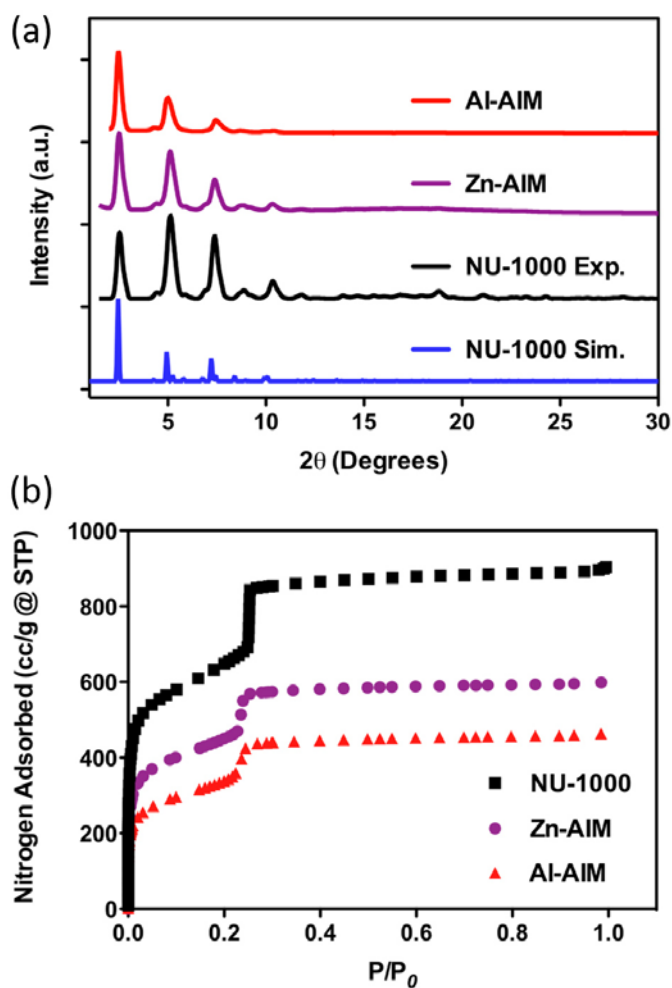


FIGURE 1. Relevant structural features and representation of NU-1000. For simplicity hydrogen atoms are not shown.

TBApy linkers. Four of the eight terminal -OH groups point into large 3.1 Å mesoporous channels, while the remaining terminal -OH groups lie in between sheets of the Zr_6 nodes. NU-1000 has a Brunauer-Emmett-Teller surface area of 2,300 $m^2 g^{-1}$ and a total pore volume of 1.4 $cm^3 g^{-1}$. In short, NU-1000 is an ideal platform for readily metallating a MOF via ALD and solution-based techniques.

NU-1000 was placed in an ALD reactor and exposed to $Al(Me)_3$ and $Zn(Et)_2$. Metallation was confirmed by inductively coupled plasma optical emission spectroscopy; on average eight Al and four Zn atoms per $Zr_6(\mu_3-OH)_8(-OH)_8$ node were incorporated into NU-1000. The resultant materials have been termed Zn-AIM and Al-AIM. Very similar metal loadings can also be obtained by depositing $Al(Me)_3$ and $Zn(Et)_2$ from solution. Powder X-ray diffraction (PXRD) (Figure 2a), N_2 adsorption isotherms (Figure 2b), diffuse reflectance infrared Fourier transform spectroscopy



STP - standard temperature and pressure

FIGURE 2. (a) PXRD patterns of NU-1000 simulated (Sim.) from the crystallographically solved structure, NU-1000 experimental (Exp.), Zn-AIM, and Al-AIM. (b) Pore size distributions and N_2 adsorption isotherms for NU-1000, Zn-AIM and Al-AIM.

and scanning electron microscopy-energy dispersive X-ray characterization confirmed that metallation occurs at the $Zr_6(\mu_3-OH)_8(-OH)_8$ node and that the NU-1000 framework is robust to the ALD treatment. These are extremely high metal loadings in the context of typical metal loadings within MOFs and in principle should lead to higher H_2 storage capacities at or close to room temperature.

Next we moved to utilizing ALD to deposit Cu cations within NU-1000, on average we observe eight Cu atoms per $Zr_6(\mu_3-OH)_8(-OH)_8$ node. PXRD, N_2 adsorption isotherms and diffuse reflectance infrared Fourier transform spectroscopy again confirmed the integrity of the material. The surface area normalized H_2 uptake is shown in Figure 3a, the Cu-AIM sample uptakes more H_2 at 77 K, per unit surface area, than the parent MOF NU-1000. Temperature-dependent H_2 isotherms were collected (Figure 3b) and Q_{st} were extracted utilizing either single- or dual-site Langmuir adsorption isotherm models followed by Clausius-Clapeyron analysis. The Cu-AIM sample shows a 60% increase in Q_{st} over the parent MOF (Figure 3c), albeit at only ~ 7 kJ/mol. The results demonstrate the ability of ALD to incorporate metal sites capable of more strongly binding molecular H_2 and without having to remove solvent or other ligated molecules.

CONCLUSIONS AND FUTURE DIRECTIONS

Conclusions

- A robust $-OH$ functionalized Zr_6 -based sorbent, NU-1000, has been synthesized and characterized
- NU-1000 has been metallated via ALD and solution
- A 60% increase in Q_{st} is observed

Future Directions

- Optimize ALD metallations
- Explore additional ALD chemistry, including metal-oxide/hydroxide clusters
- Materials characterization and performance

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Mondloch, J.E.; Bury, W.; Farha, O.K.; Hupp, J.T. “Gas-Phase Deposition by Atomic Layer Deposition in Metal–Organic Frameworks” Invention disclosure, submitted.

FY 2013 PUBLICATIONS/PRESENTATIONS

1. Mondloch, J.E.; Bury, W.; Fairen-Jimenez, D.; Kwon, S.; DeMarco, E.J.; Weston, M.H.; Sarjeant, A.A.; Nguyen, S.T.; Stair, P.C.; Snurr, R.Q.; Farha, O.K.; Hupp, J.T. “Vapor-Phase Metalation by Atomic Layer Deposition in a Metal–Organic Framework” *J. Am. Chem. Soc.* **2013**, *135*, 10294.

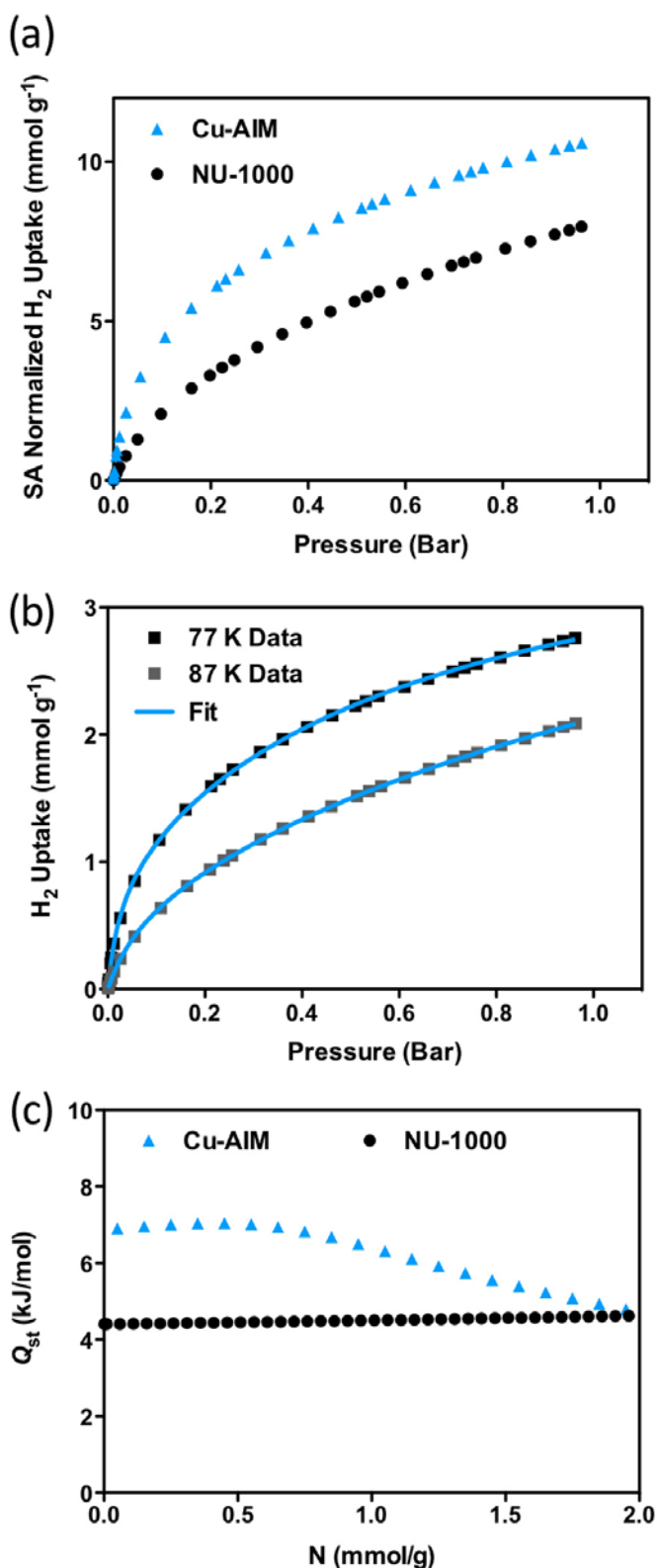


FIGURE 3. (a) Surface area normalized H_2 adsorption of NU-1000 and Cu-AIM. (b) Temperature-dependent H_2 sorption for Cu-AIM and fits to a dual-site Langmuir model. (c) Q_{st} for NU-1000 and Cu-AIM.

2. Mondloch, J.E.; Farha, Bury, W.; Farha, O.K.; Hupp, J.T. “*Metal- and Cluster-Modified Sorbents for the Ambient Temperature Storage of Molecular Hydrogen*” Presented at Annual DOE EERE Postdoctoral Research Award Meeting, Golden, CO, 2013.
3. Mondloch, J.E.; Bury, W.; Farha, O.K.; Hupp, J.T. “*Metallation by Atomic Layer Deposition In A Metal–Organic Framework (AIM)*” ALD-AVS 2013, San Diego, CA, 2013.

REFERENCES

1. Getman, R.; Miller, J.; Wang, K.; Snurr, R. “Metal Alkoxide Functionalization in Metal-Organic Frameworks for Enhanced Ambient-Temperature H₂ Storage” *J. Phys. Chem. C* **2011**, *115*, 2066.
2. Mondloch, J.E.; Bury, W.; Fairen-Jimenez, D.; Kwon, S.; DeMarco, E.J.; Weston, M.H.; Sarjeant, A.A.; Nguyen, S.T.; Stair, P.C.; Snurr, R.Q.; Farha, O.K.; Hupp, J.T. *J. Am. Chem. Soc.* **2013**, *135*, 10294.
3. Sumida, K.; Stück, D.; Mino, L.; Chai, J.-D.; Bloch, E.D.; Zavorotynska, O.; Murray, L.J.; Dincă, M.; Chavan, S.; Bordiga, S.; Head-Gordon, M.; Long, J.R. *J. Am. Chem. Soc.* **2012**, *135*, 1083.