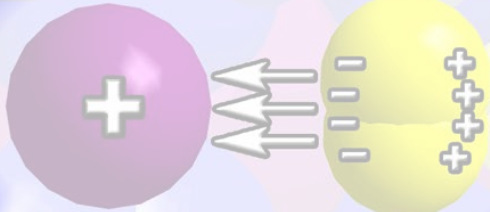
2013 DOE Hydrogen and Fuel Cells Program Review

Hydrogen Storage in Metal-Organic Frameworks



P. I. Jeffrey Long

Presenter Craig Brown

Lawrence Berkeley Nat. Lab., Univ. of California Berkeley
Nat. Inst. of Standards and Technology, General Motors Co.

May 15, 2013

Project ID #: ST103

This presentation does not contain any proprietary, confidential, or otherwise restricted information

BERKELEY LAB NLST GM U.S. DEPARTMENT OF ENERGY Energy Efficiency & Renewable Energy

Overview

Timeline

- Start: April 2012
- Finish: March 2015
- 30% complete

Budget

- Total project funding
  - DOE share: $2,100k
  - Contractor share: $525k
- Funding received in FY12:
  - $500k
- Funding planned for FY13:
  - $600k

Barriers

- Barrier addressed
  - A. System Weight and Volume

Partners

- LBNL: synthesis and modeling
- NIST: neutron diffraction (start Oct. 2012)
- GM: high-pressure adsorption (start July 2012)
- Project lead: Jeffrey Long (LBNL)

Relevance

Project objectives

- Research and development of on-board systems that allow for a driving range greater than 300 miles.

- Materials sought with the potential for meeting the DOE targets of reversible uptake:
  - 2017 targets: 5.5 % H_2 by mass, volumetric capacity of 40 g/L
  - "ultimate full fleet" targets: 7.5 % H_2 by mass, 70 g/L.

- Synthesize new metal-organic frameworks capable of achieving the –20 kJ/mol adsorption enthalpy required for use as hydrogen storage materials operating under 100 bar at ambient temperatures

Approach

Task 1: Synthesis of Metal-Organic Frameworks
(Jeffrey Long-LBNL)

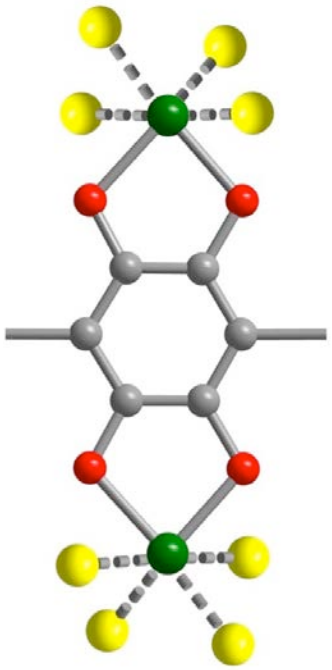
Task 2: Characterization of Framework-H_2 Interactions
(Craig Brown-NIST)

Task 3: First-Principles Calculations of Hydrogen Binding Enthalpies
(Martin Head-Gordon-LBNL)

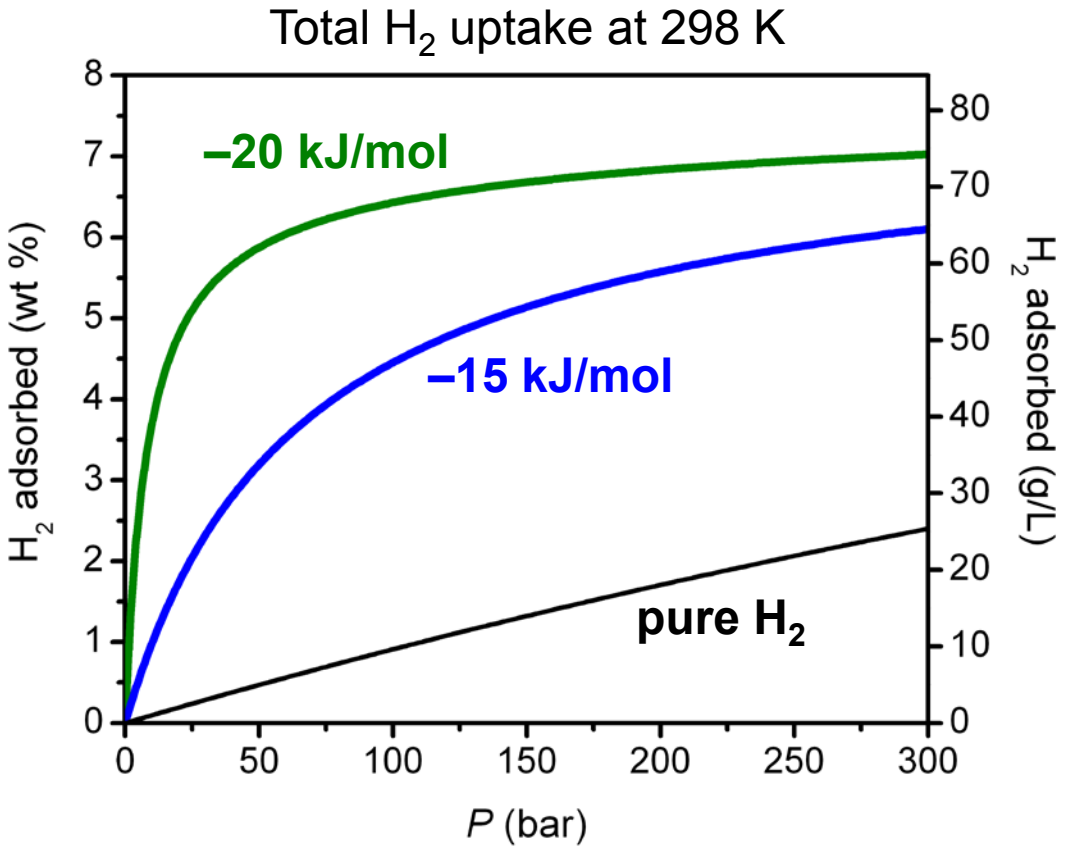
Task 4: High-Pressure H_2 Adsorption Measurements
(Anne Dailly-GM)

Approach

Multiple H_2 Binding Sites per Metal



$Al(OH)(C_{14}O_{12}Mg_4)$

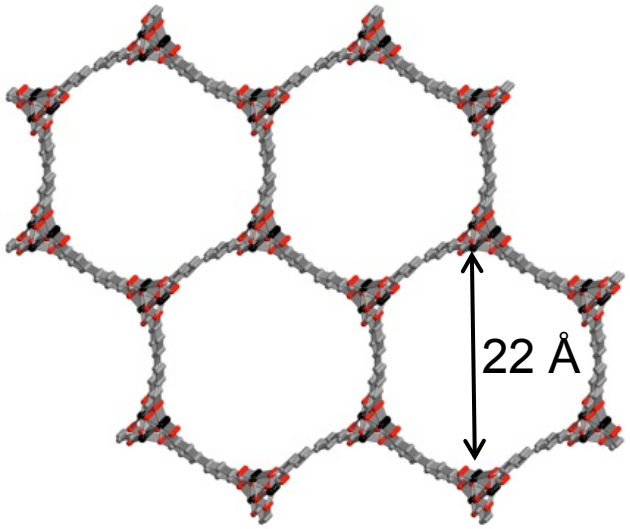


- Isotherms simulated using dual site Langmuir model with estimated parameters
- Binding enthalpy and associated entropy not yet known for Mg^{2+} in this geometry

Approach: Milestones and Go/No go

Due date	Description	% Comp	Status March 2013
03/13	**Go/No-go (Task 1):** Demonstration of ability to prepare 5 mixed functionality ligands allowing for post-synthetic insertion of metal cations	100%	7 ligands containing both carboxylate and pyridine/phenol binding sites have been prepared
03/13	**Go/No-go (Task 1)**: Development of in silico screening for calculating opposing pore surface distances	100%	Software completed and manuscript submitted
03/13	**Go/No-go (Task 1):** Preparation of two new MOFs containing coordinatively-unsaturated high-valent cations.	100%	Frameworks with open Al^{3+} and Ti^{3+} sites have been synthesized
03/13	**Milestone (Task 2):** Demonstrated ability to locate and uncover detailed descriptions of high-enthalpy H_2 binding sites in high-valent MOFs via neutron diffraction	30%	Diffraction measurements on pyridine and MOF-74 variants performed. Analysis underway
03/13	**Milestone (Task 3):** Demonstration of a correlation between calculated and experimentally observed H_2 binding affinities and usefulness in facilitating design of new materials	100%	Calculated H_2 binding parameters agree with experimental values
03/13	**Milestone (Task 4):** Demonstrate ability to accurately measure H_2 adsorption in MOFs at 298 K and pressures up to 350 bar	30%	High-pressure system installed and some benchmark samples measured

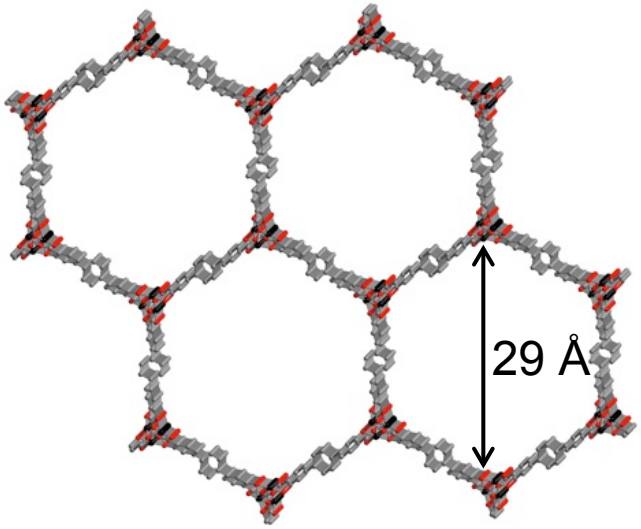
Accomplishments: Task 1
Synthesis of Expanded MOF-74 Analogues



M_2(dobpdc)

(M = Mg, Mn, Fe, Co, Ni, Zn)

SA_{Lang} = 2700-3500 m^2/g



M_2(dotpdc)

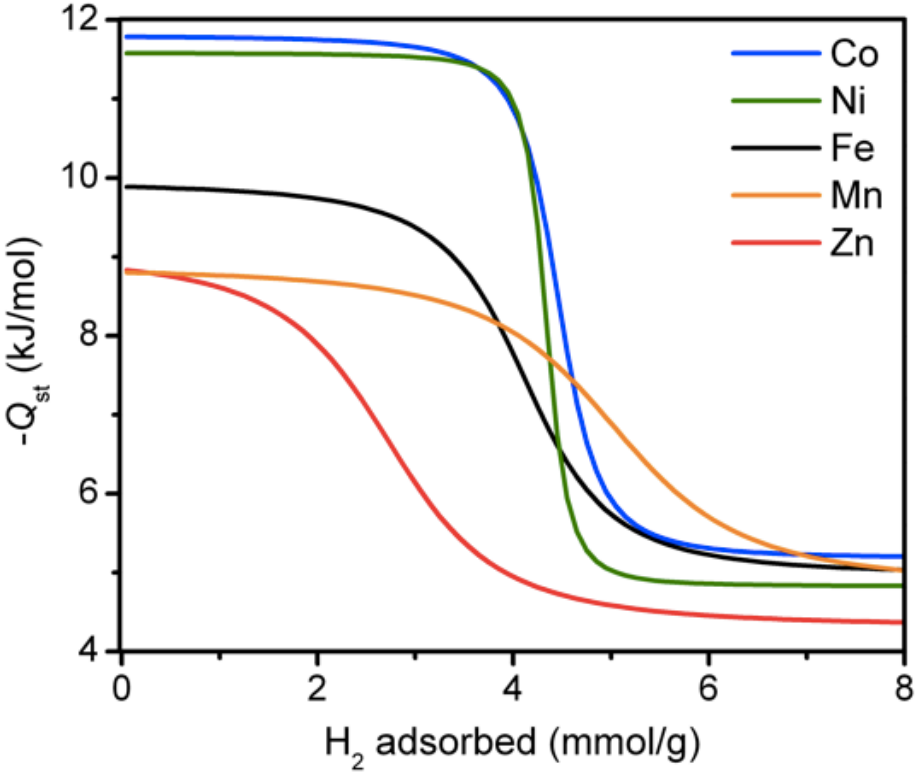
(M = Mg, Mn, Fe, Co, Ni)

SA_{Lang} = 3500-4800 m^2/g

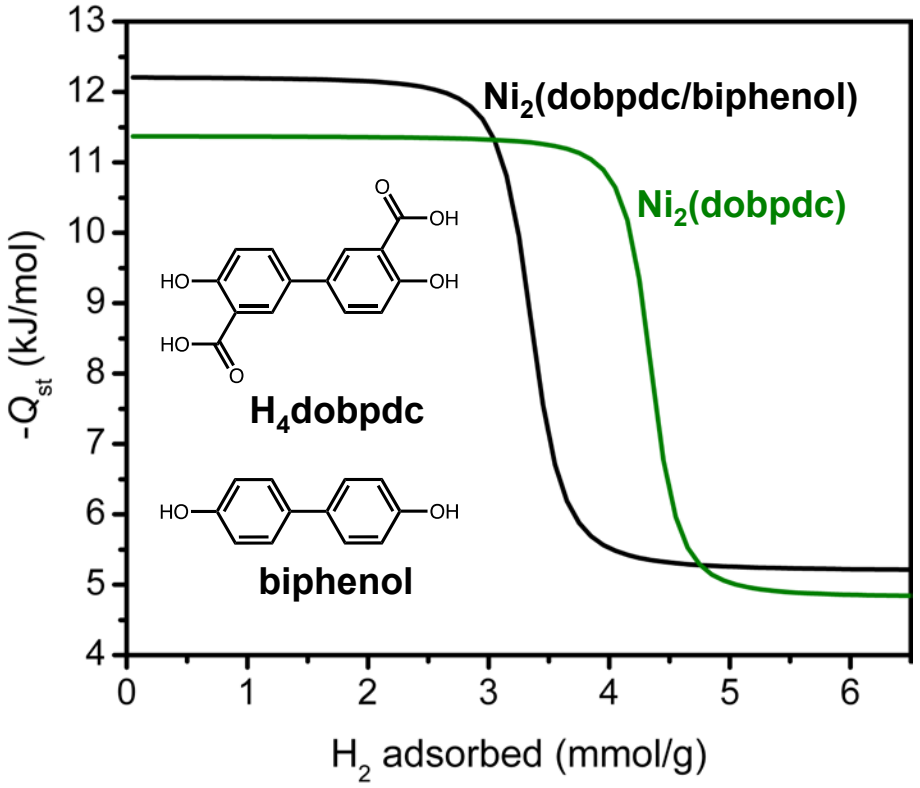
- Higher surface areas and pore sizes will allow systematic study of high-pressure adsorption
- Robust framework and extra volume to accommodate analogous ligands that can support highly exposed metal cations

Accomplishments: Task 1

Isosteric Heats of H_2 Adsorption in M_2(dobpdc)



The Co^{2+} and Ni^{2+} analogues display H_2 binding enthalpies approaching -12 kJ/mol



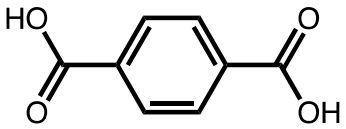
H_2 binding enthalpies can be increased through the introduction of defect sites

Accomplishments: Task 1

Synthesis of M^{3+}-Based Metal-Organic Frameworks

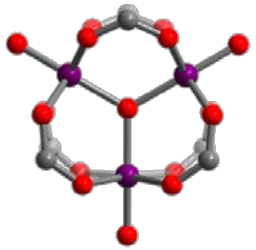
$TiCl_3$

+



DMF, EtOH

1 day, 120°C

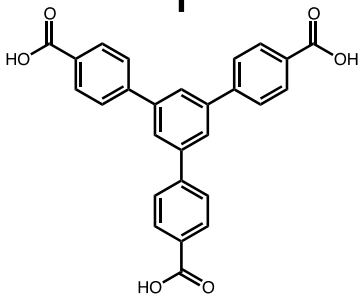


$Ti_3O(BDC)_3Cl(DMF)$

SA_{BET} = 2570 m^2/g

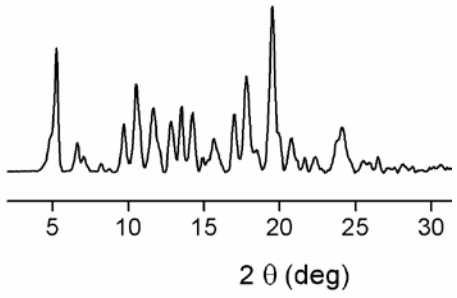
$AlCl_3$

+



DMF, HCl

1 day, 120°C



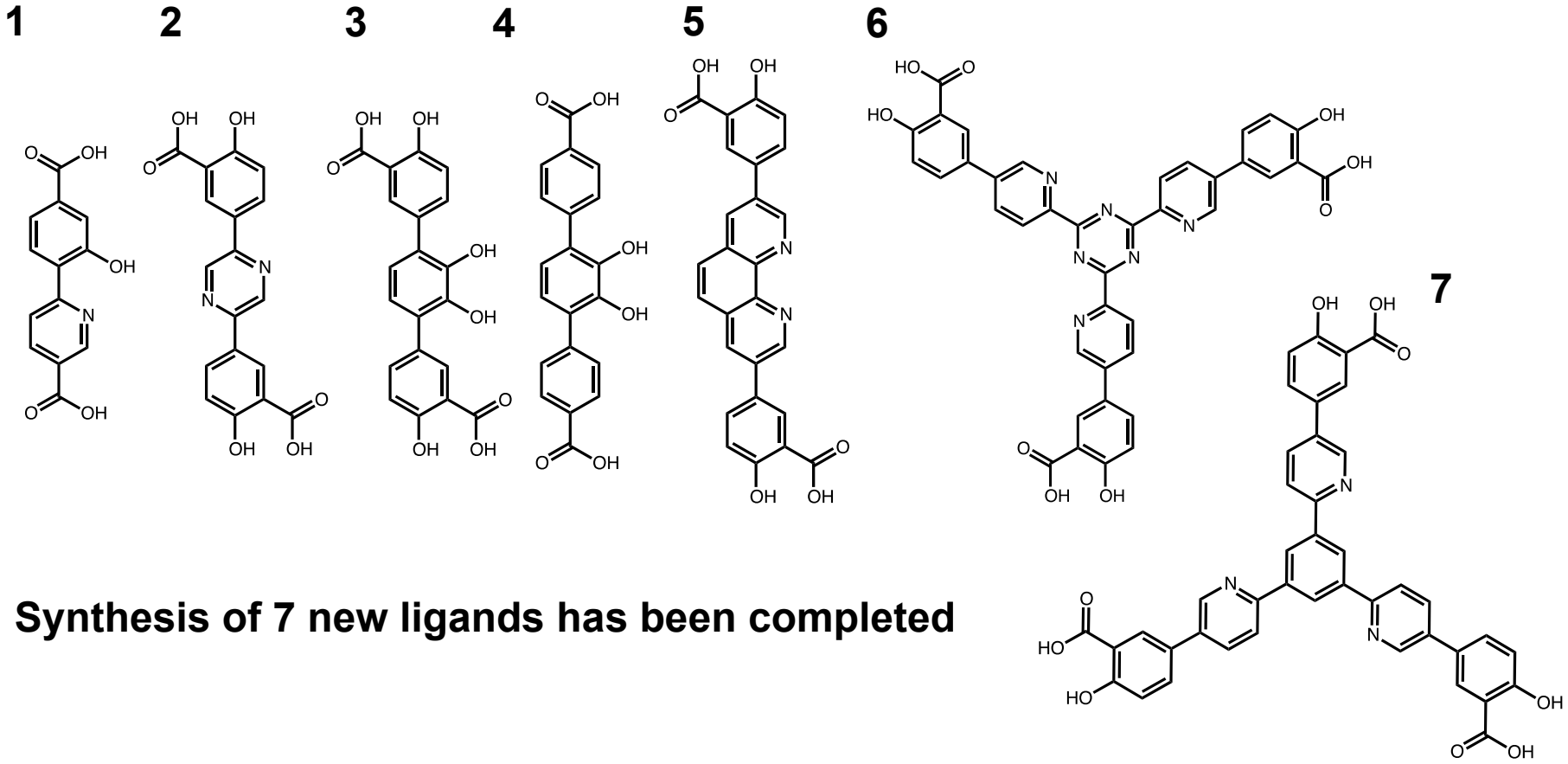
Al-BTB

SA_{BET} = 3250m^2/g

Two new frameworks displaying the highest reported surface areas for Ti^{3+} and Al^{3+} MOFs have been synthesized

Accomplishments: Task 1

Synthesis of Mixed Functionality Ligands

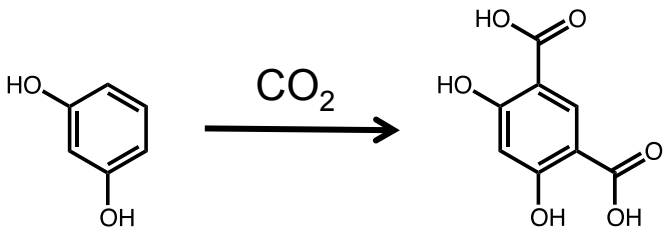


Synthesis of 7 new ligands has been completed

Incorporation of these ligands into metal-organic frameworks is ongoing. Porous, crystalline phases have been identified for 1,2,4,5.

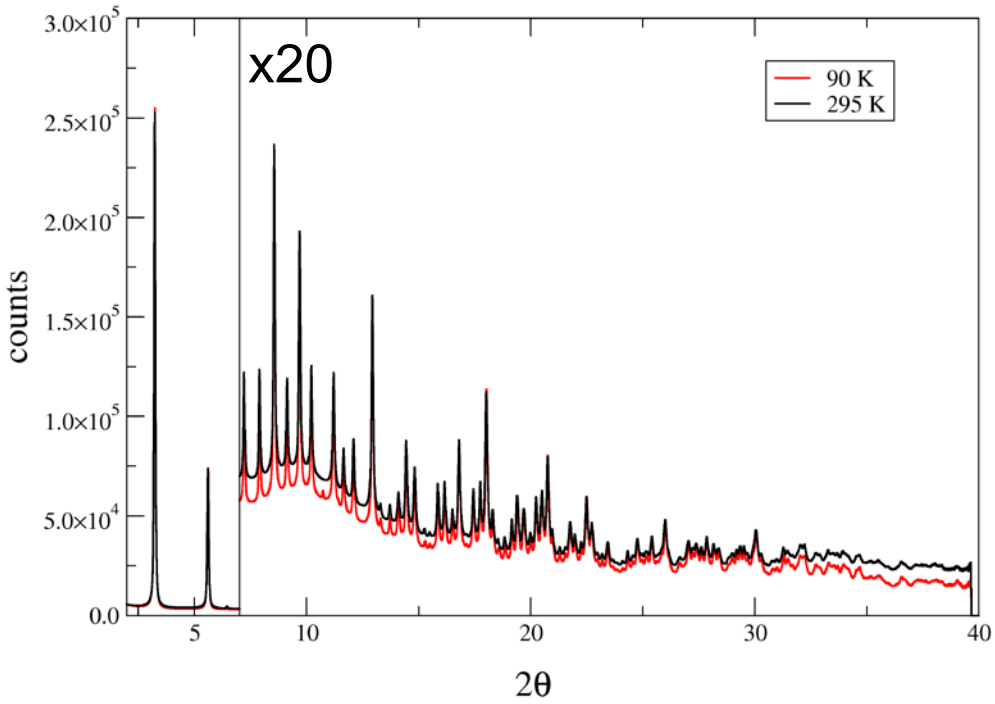
Accomplishments: Task 2
Powder Diffraction of Cobalt and Nickel MOFs

Newly synthesized cobalt and nickel MOFs



H_4dobdc'

M_2(dobdc') (M = Co, Ni)
SA_{Lang} = 1400-2000 m^2/g

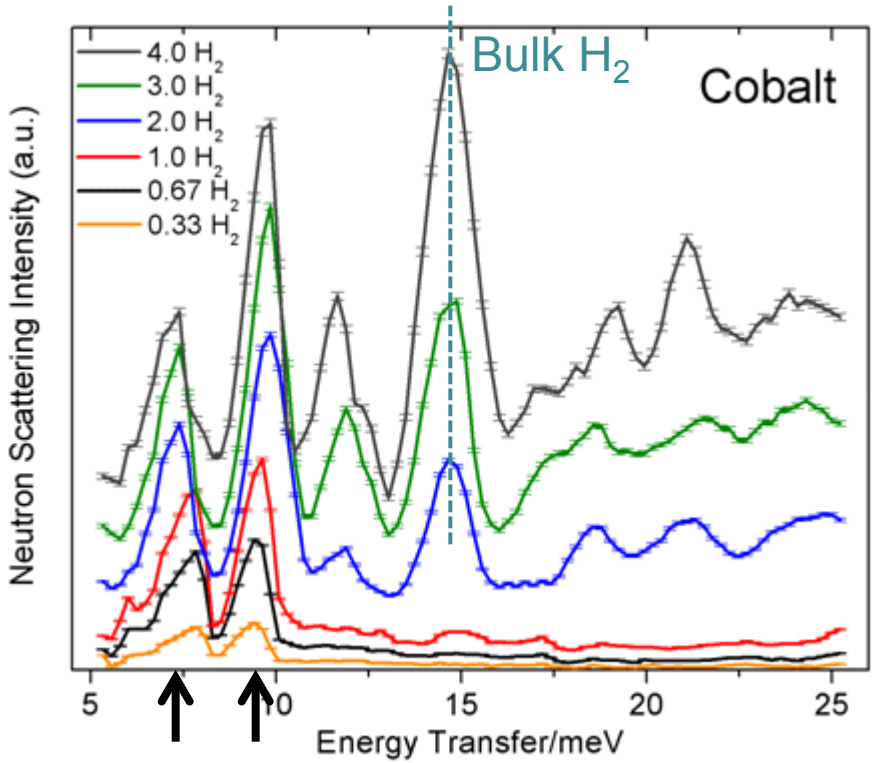


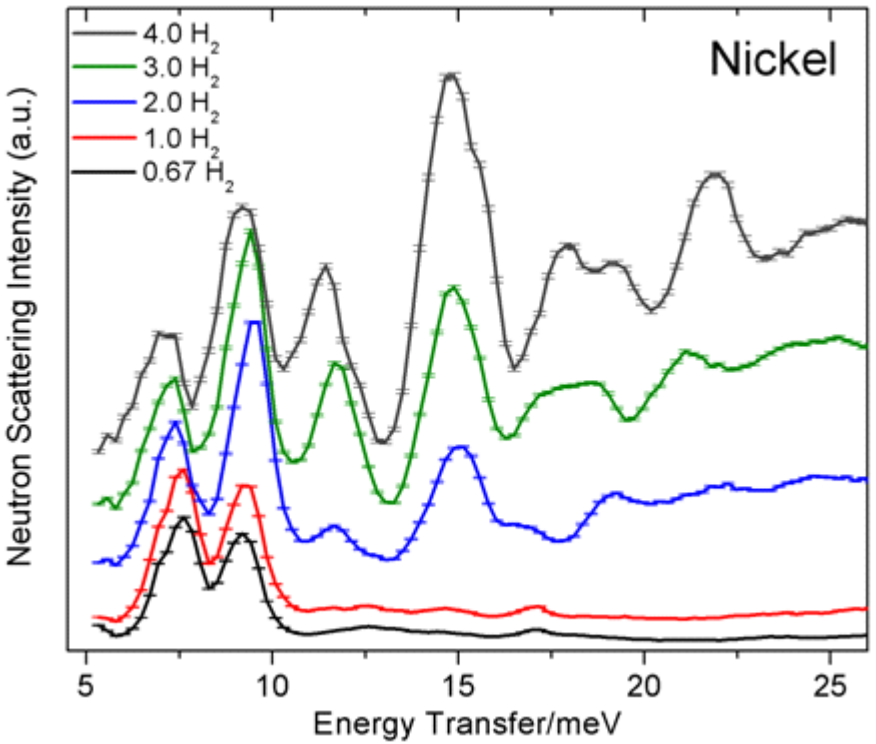
X-ray and neutron powder diffraction provides MOF structure and H_2 adsorption sites (determined crystal structure/analysis in progress)

measurements performed at APS (XRS) and NIST (neutrons)

Accomplishments: Task 2

Neutron Inelastic Scattering of Cobalt and Nickel MOFs

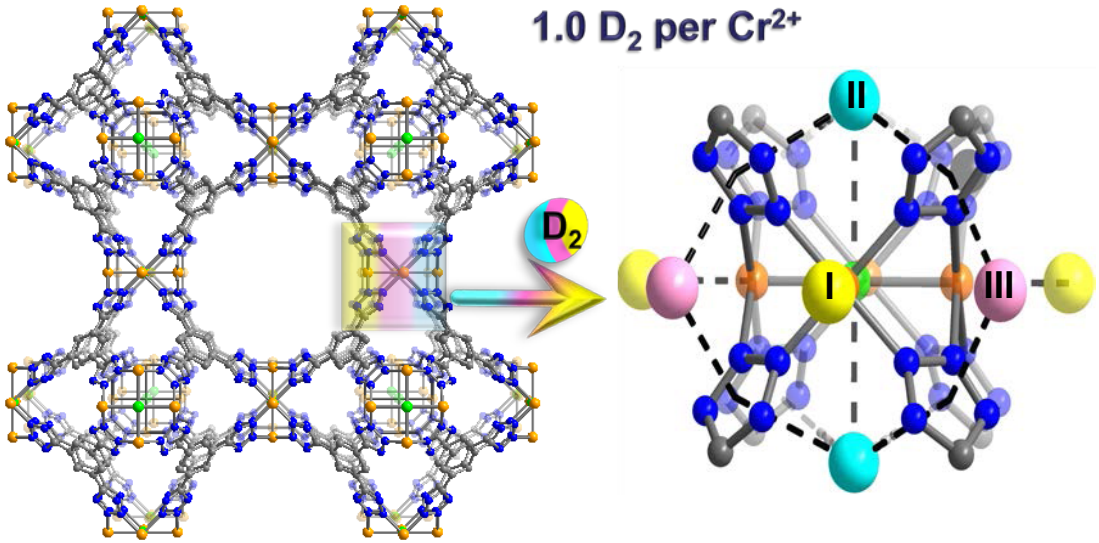




- Distribution of highly active sites shifts H_2 rotational lines away from bulk line
- At least three different adsorption sites identified, becoming more 'bulk'-like by ~3H_2:metal loadings.

measurements performed at NIST

Accomplishments: Task 2
Determination of Cr-BTT structure



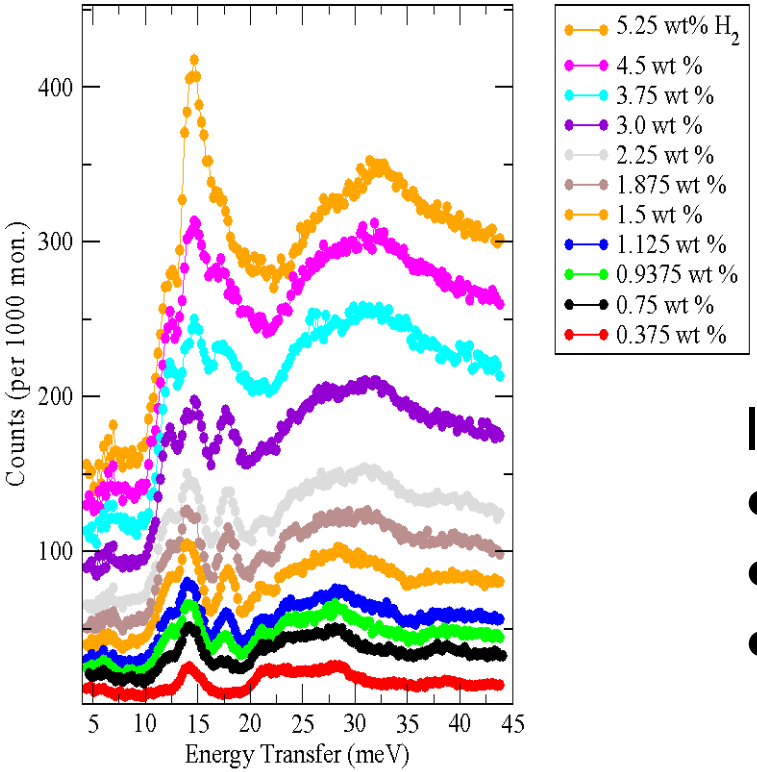
Bond	distance(Å)
Cr-Cl	2.42(4)
Cr-N	2.075(8)
Cr-D(I)	2.64(6)
Cl-D(II)	3.56(3)

Structure determination

- Correlate enthalpy to structure / electronic configuration of TM
- Feeds into calculations

Accomplishments: Task 2

Determination of Co-BTT:H_2 adsorption potential

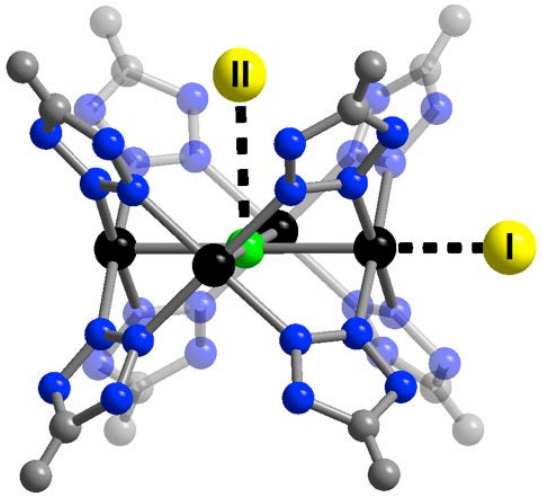


Inelastic neutron scattering of H_2 provides

- Determination of binding strength
- Loading dependence of different sites
- Strict comparison for theory

Accomplishments: Task 3

Calculations on Cu-BTT: Structure



Bond (Å)	exp.[b]	calc.
M–Cl	2.504	2.456
M–N(1)	2.007	2.040
N(1)–N(1)	1.344	1.323
N1–N(2)	1.323	1.310
N(2)–C	1.354	1.332

Angle (°)	exp.[b]	calc.
Cl–M–N(1)	87.0	89.5
M–N(1)–N(1)	123.2	121.8
M–N(1)–N(2)	127.0	128.2
N(1)–N(2)–C	104.3	103.8
N(2)–C–N(2)	111.7	112.6

Structure prediction

- Pre-requisite for H_2 binding

DFT calculations using ωB97X-D

- Near-quantitative agreement
- JACS 135, 1083 (2013)

Accomplishments: Task 3
Calculations on M-BTT: H_2 binding

DFT calculations of H_2 binding are sensitive to functional used

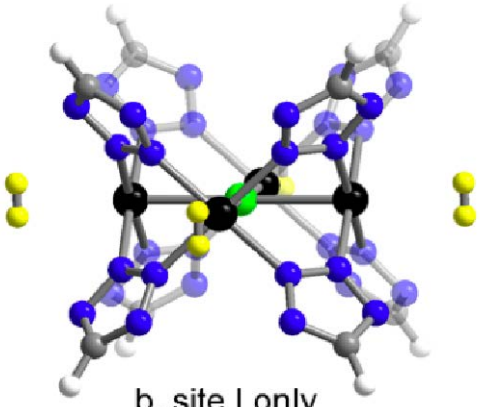
- ZPE and BSSE corrections are used for all calculations
- LDA, GGA (BP86) and hybrid (B3LYP) show large errors
- The range-separated dispersion-corrected functional (ωB97X-D) is quite accurate

functional	Mn: HBE (kJ/mol)	Cu: HBE (kJ/mol)
LDA	-27.2	-18.9
BP86	-0.7	3.1
B3LYP	-2.7	1.3
ωB97X-D	-14.9	-9.4
exp.	-11.9	-10.4

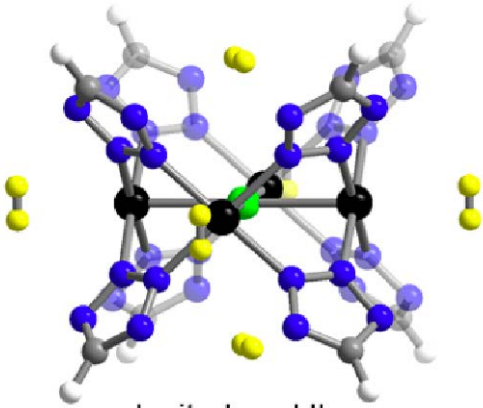
JACS 135, 1083 (2013)

Accomplishments: Task 3

Calculations on M-BTT: M…H_2 & IR



b. site I only



d. site I and II

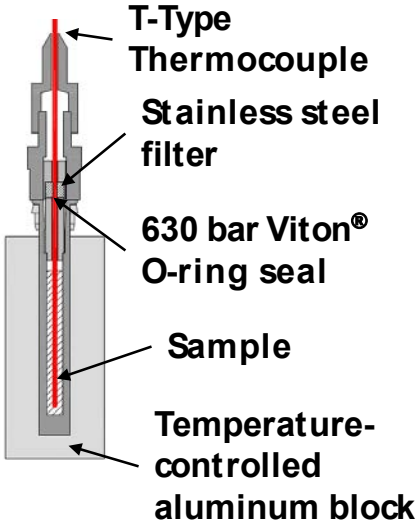
		M = Mn		Cu		Zn
		calc.	exp.	calc.	exp.	calc.
HBE (kJ/mol)	site I only	−14.9	−11.9[a]	−9.4	−10.4[a]	−14.0
	site II only	−7.4		−6.9		−7.6
	site I + II	−11.0	−10.3[b]	−8.5	−9.5[b]	−11.5
H_2 distance (Å)	M···H_2 (site I)	2.33	2.27[c]	2.56	2.47[c]	2.27
	Cl···H_2 (site II)	3.25	3.47[c]	3.20	3.46[c]	3.22
$\Delta\nu$ (cm^{-1})	site I	−125	−123[a]	−78	−100[a]	−129
	site II	−16	−31[a]	−14	−41[a]	−16

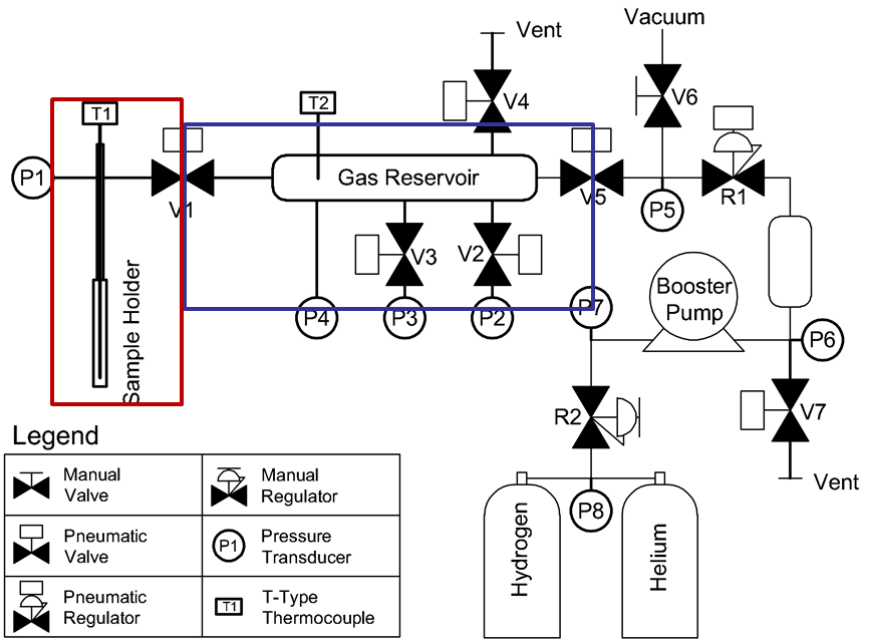
[a]Based on infrared data; [b]Zero-coverage isosteric heat of adsorption; [c]Based on neutron diffraction data.

Calculated H_2 binding parameters agree with experimental values and can be used to explore possible new materials

Accomplishments: Task 4

High-Pressure H_2 Adsorption System





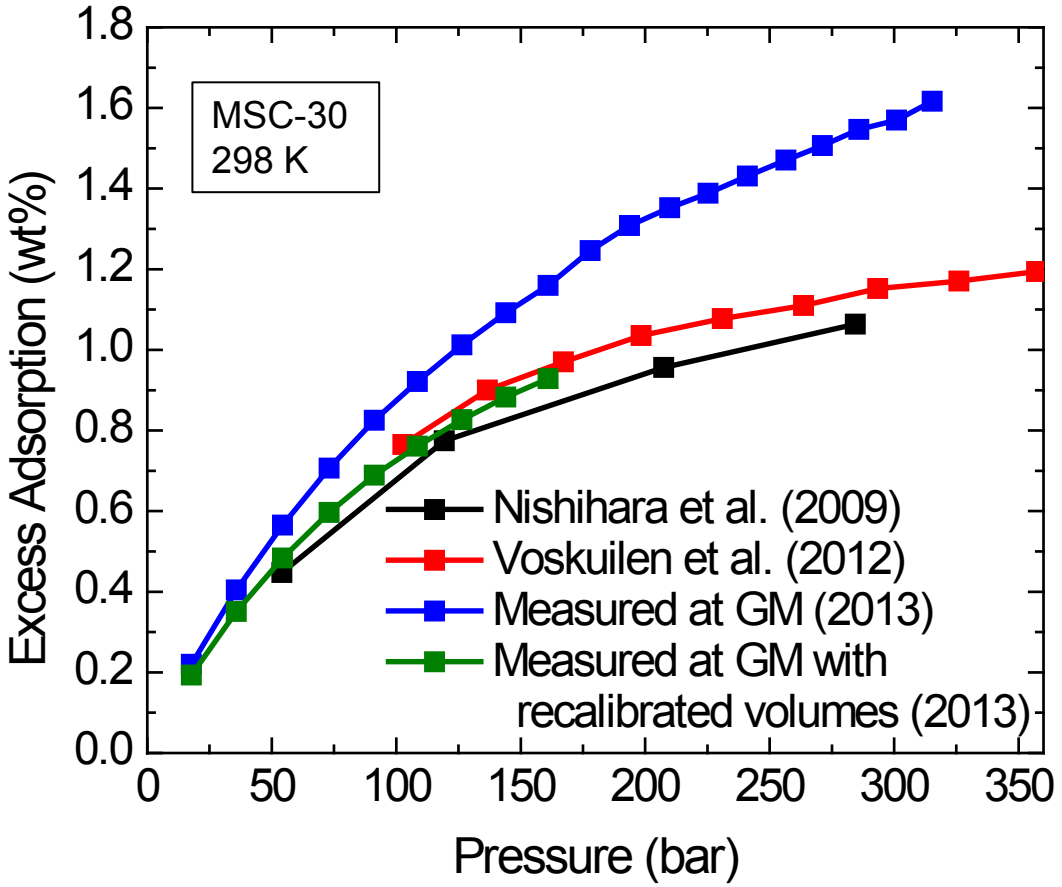
Challenges of 350 bar H_2 measurements:

- System needs to be calibrated very well to minimize uncertainty
- 0.05 cm^3 reference volume error
  → ~500 µmol deviation at 350 bar
- 0.5 g of MSC-30 adsorbs ~3000 µmol at 350 bar and 298 K
- Volumes needed recalibration after installation

- Max operating pressure: 344 bar
- Thermoelectric temperature control
- Large sample capacity (~500 mg)

Accomplishments: Task 4
Evaluation of Benchmark Materials

- Benchmark materials MSC-30 & MOF-177 measured for instrument validation
- Measurements taken after recalibration show good agreement with previous results (agreement is within uncertainty)
- High-pressure (>180 bar) range still needs to be recalibrated



Collaborations

Project team within DOE Fuel Cell Technologies Office:

- Lawrence Berkeley National Laboratory (prime, National Lab.)/UC Berkeley:
  - Jeffrey Long: Synthesis and basic characterization of MOFs
  - Martin Head-Gordon: Calculation and prediction of H_2 binding energies
- National Institute of Standards and Technology (sub, National Lab.):
  - Craig Brown: Neutron diffraction and neutron spectroscopy
- General Motors Company (sub, Industry):
  - Anne Dailly: Measurement of high-pressure H_2 uptake capacity

Additional collaborations:

- Oberlin College (University):
  - Stephen Fitzgerald: Infrared spectroscopy
- Purdue University (University):
  - Timothée Pourpoint: Development of high-pressure H_2 adsorption system

Proposed Future Work

Task 1: Synthesis of Metal-Organic Frameworks

- Continue structural characterization of Al-BTB and $Ti_3O(BDC)_3$
- Scale up synthesis of bipyridine containing MOFs and insert metal cations
- Use *in silico* screening technique to discover new materials with optimal opposing surface distances
- Complete synthesis of catechol and biphenol type ligands and prepare new MOFs with these ligands containing post-synthetically inserted ligands

Task 2: Characterization of Framework-H_2 Interactions

- Solve structure for new Co-MOF74'
- Understand structural loading dependence with H_2
- Complete Milestone for demonstrating utility of techniques
- Obtain newest MOFs from Long Group
- Perform diffraction measurements on most promising candidates, to give feedback on highest adsorption sites to partners

Proposed Future Work

Task 3: First-Principles Calculations of Hydrogen Binding Enthalpies

- Modifications to Al(OH)bpydc (MOF-253) based on metal insertions at the bpy binding site. Explore H_2 binding in this system as a function of metal and counter ions, and linker modifications
- Exploring metal insertions in deprotonated catechols. What are the solvent binding energies (for desolvation)? Make reliable H_2 binding predictions for complete and partial desolvation
- Design principles for target H_2 binding energies. Identify the relevant descriptors as a basis for rational design

Task 4: High-Pressure H_2 Adsorption Measurements

- Further validate high-pressure H_2 adsorption in metal-organic frameworks and compare results to theoretical and spectroscopic predictions
- Modify instrument program and test commercially available (benchmark) MOF samples for 20-30 cycles up to 350 bar
- Test high performing MOFs for 100 cycles up to 350 bar

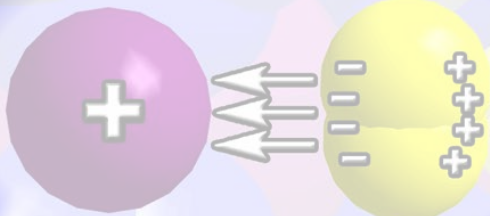
Summary

- A variety of expanded MOF-74 analogues, showing high surface area and high H_2 binding enthalpies have been synthesized
- Neutron powder diffraction and inelastic scattering have been utilized to solve new structures and characterize the strength of M^{2+}-H_2 interactions
- Calculated H_2 binding enthalpies show excellent agreement with experimental values
- High-pressure adsorption system validated, calibrations are ongoing
- The combination of theoretic predictions, synthetic work, and structural characterization will be used to prepare new frameworks with a larger density of strong H_2 binding sites

Capacity	2012	2013	2017*	Ultimate*
Gravimetric	0.016 kg H_2/kg adsorbent	0.016 kg H_2/kg adsorbent	0.055 kg H_2/kg system	0.075 kg H_2/kg system
Volumetric	0.011 kg H_2/L adsorbent	0.011 kg H_2/L adsorbent	0.040 kg H_2/L system	0.070 kg H_2/L system

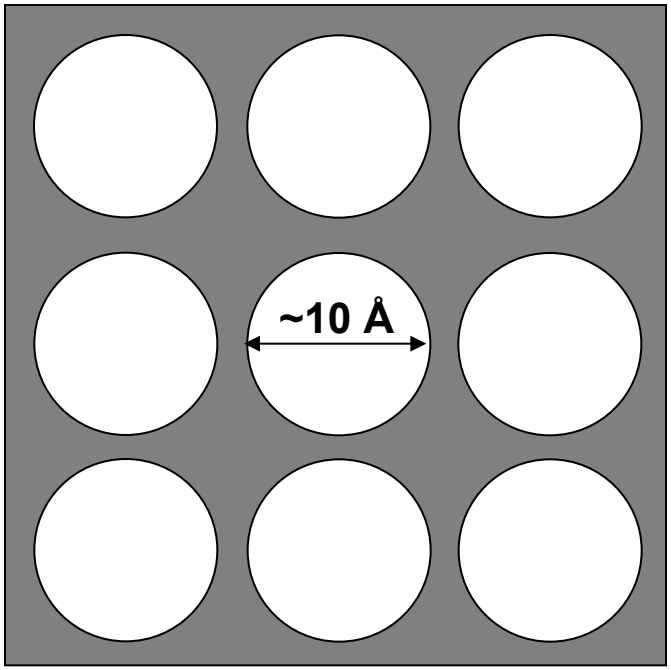
*DOE targets

Technical Back-Up Slides

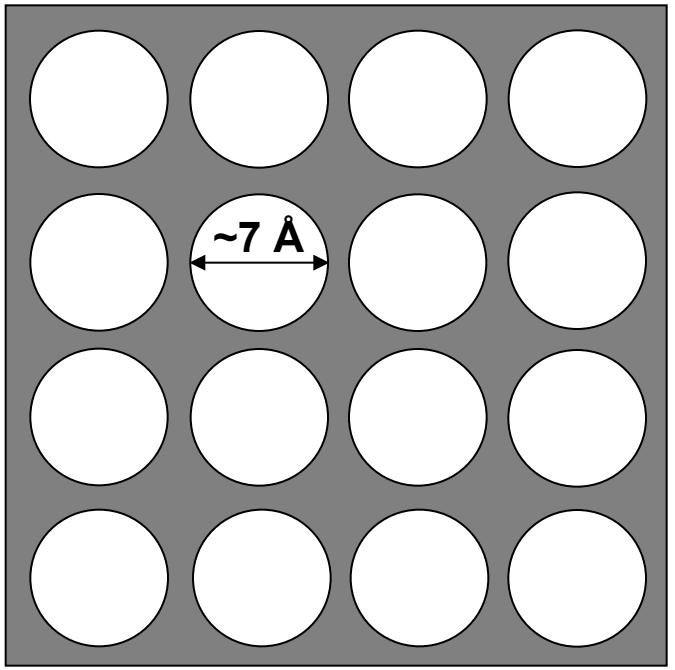


Optimum Pore Sizes for Hydrogen Storage

77 K



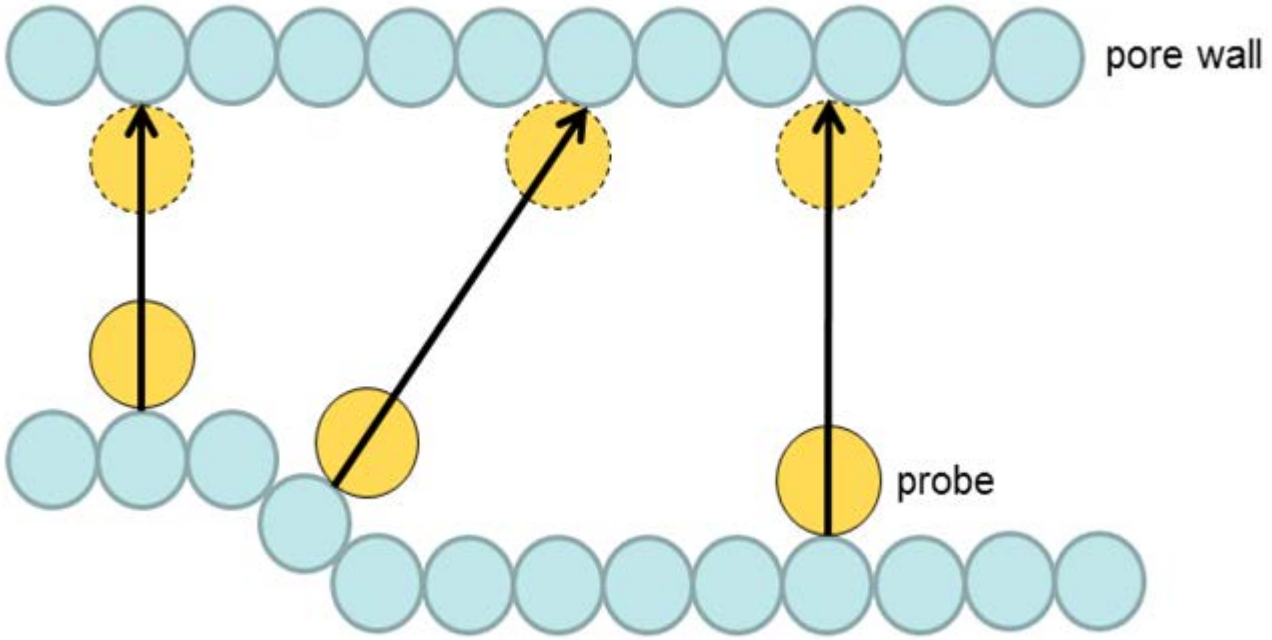
298 K



- Calculated using Monte Carlo simulations with both cylindrical and slit pores

Rzepka, Lamp, de la Casa-Lillo J. Phys. Chem. B ***1998**, 102, 10894*

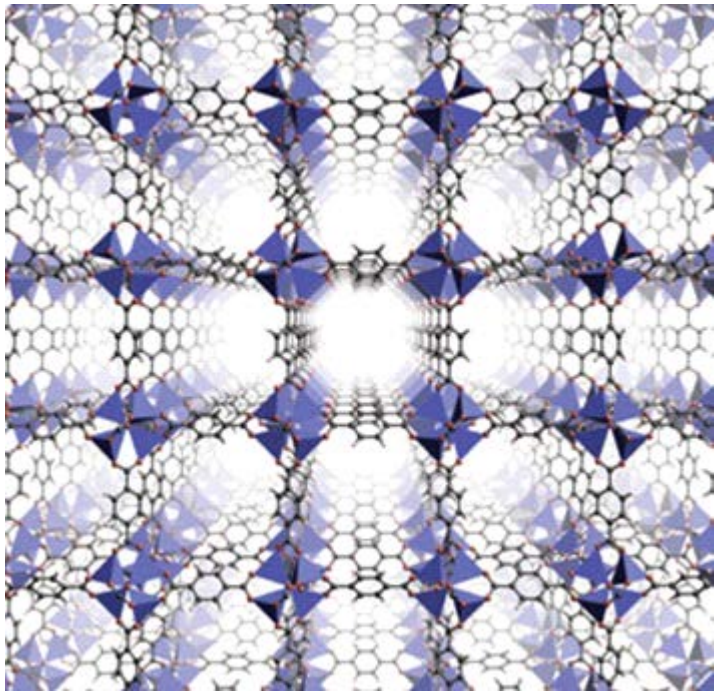
Geometric Calculation of Opposing Wall Distances



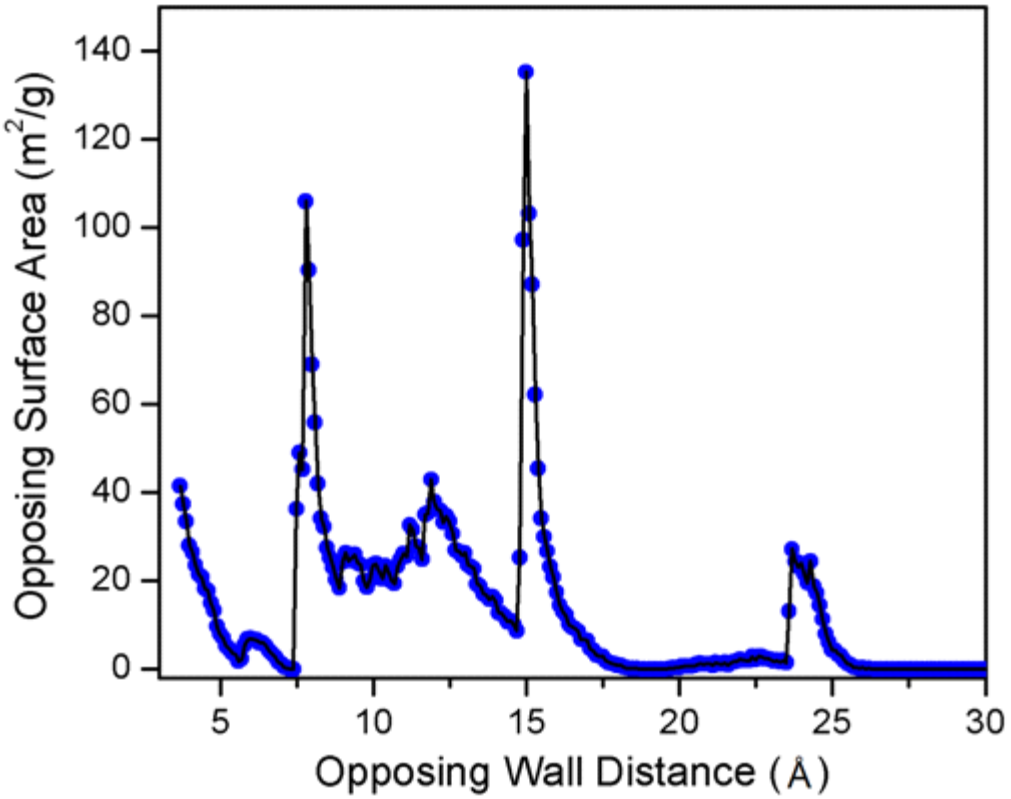
- Probe is inserted on the pore surface, and moved away in a direction normal to the surface until it collides with the opposing wall
- This is repeated until the entire pore surface has been traversed by the algorithm to create a distribution of opposing wall distances

Sumida, Rogow, Herm, Long, submitted

Opposing Surface Area Distribution (OSAD)



MOF-5



Sumida, Rogow, Herm, Long, submitted

Synthesis of M_2(dobpdc)