2014 DOE Hydrogen and Fuel Cells Program Review

Hydrogen Storage in Metal-Organic Frameworks

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Project ID #: ST103

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Overview

Timeline

- Start: April 2012
- Finish: March 2015

Budget

- FY13 DOE Funding:
  - $600k
- Planned FY14 DOE Funding:
  - $700k
- Total project funding
  - Total Project Value: $2,625k
  - Cost Share: $525K
  - DOE Share: $2,100K
  - DOE Funding Spent*: $1,533K

    *as of 3/31/14

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 –15 to –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)

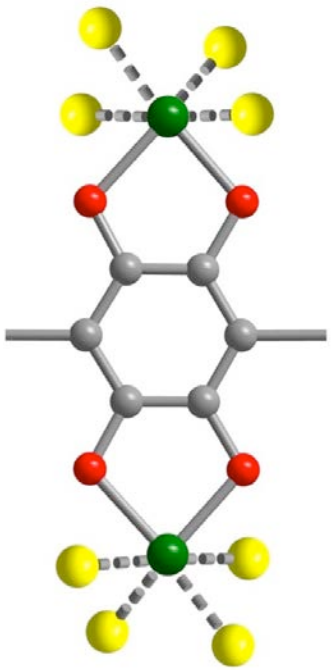
Task 2: Characterization of Framework-H_2 Interactions
(Craig Brown-NIST)

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

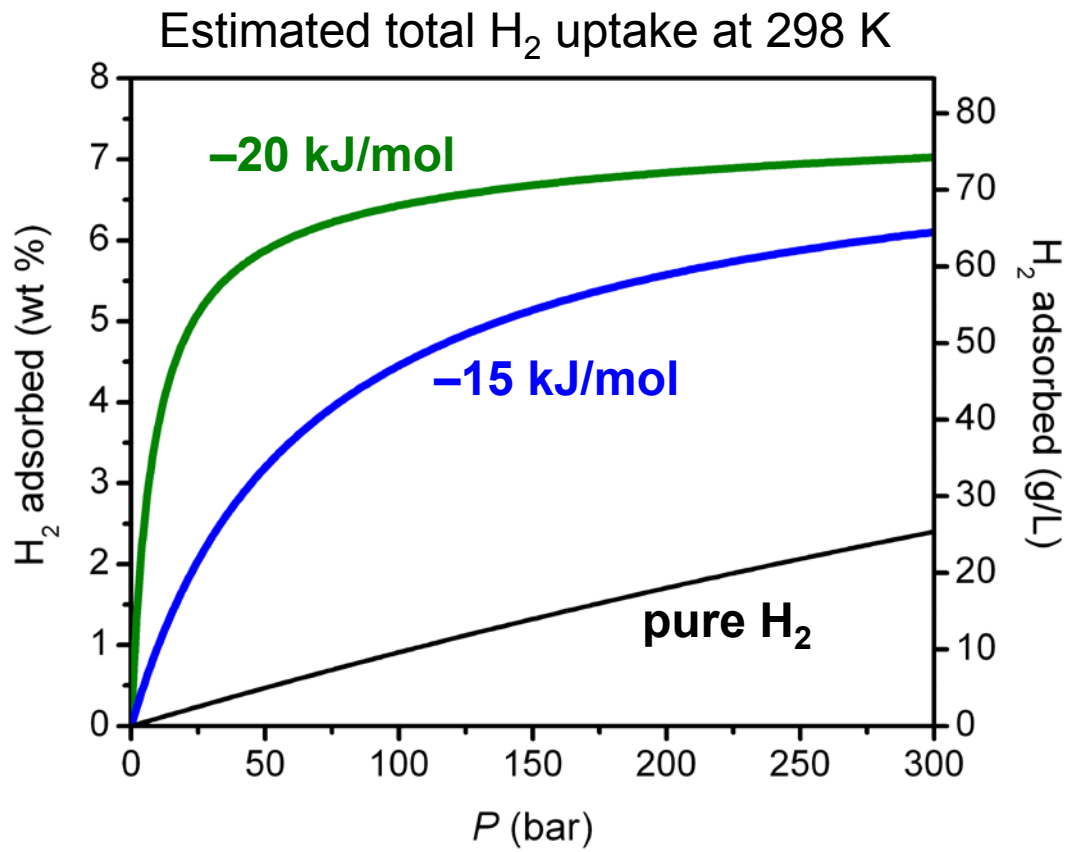
Task 4: High-Pressure H_2 Adsorption Measurements
(Anne Dailly-GM)

Approach

Multiple H_2 Binding Sites per Metal



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



- Create MOFs with exposed M^{2+} or M^{3+} cations, each binding 4 or 5 H_2 molecules
- Hypothetical MOF can meet capacity targets, depending on Mg^{2+} binding enthalpy

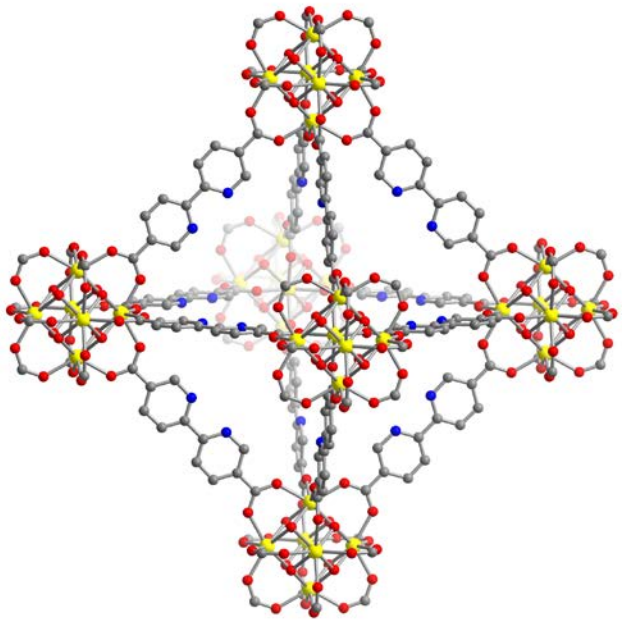
Approach: Milestones Tasks 1&2

Due date	Description	% Comp	Status April 2014
03/14	**Task 1 (G/N): Synthesis of MOFs with reversible excess H_2 uptake > 2.5 wt %**	100%	MOF-74 analogues synthesized which may surpass 2.5 wt %
03/14	**Task 1**: Preparation of a high-valent MOF with an initial H_2 adsorption enthalpy greater than 12 kJ/mol	100%	Ni_2(*m*-dobdc) displays H_2 binding enthalpy of -12.3 kJ/mol
03/14	**Task 1:** Synthesis of MOFs with the ligands prepared in year 1	100%	3 bipyridine-MOFs synthesized
03/14	**Task 1:** Demonstration of the post-synthetic insertion of metals into the open chelate sites of these new materials	100%	Single crystal diffractions shows binding of M^{2+} to the bipy sites
03/14	**Task 1:** Preparation of at least 2 MOFs with the optimal 7 Å between opposing pore surfaces as predicted with *in silico* screening	100%	3 dicarboxylate MOFs synthesized with optimal pore size
03/15	**Task 1:** Demonstration of a MOF with an initial H_2 adsorption enthalpy greater than the current record of 15.1 kJ/mol	40%	On-track
03/15	**Task 1 (G/N): Synthesis of a metal-organic framework with reversible hydrogen uptake greater than 4.5 wt % at 298 K**	30%	On-track
03/14	**Task 2:** Demonstrate that understanding of MOF-H_2 interactions through inelastic neutron scattering experiments provide new insight	90%	INS meas. on H_2 in MOF-74 variants; waiting for new materials
03/15	**Task 2:** Demonstrate the use of quasielastic neutron scattering to help understand the roles of diffusion and entropy in H_2 binding to MOFs	50%	Experiments underway; analysis underway

Approach: Milestones Tasks 3&4

Due date	Description	% Comp	Status April 2014
12/14	**Task 3:** Demonstrate the ability to determine H_2-metal interactions in realistic systems containing low-coordinate metal cations	25%	Calculation performed for catechol and bipyridine systems
03/15	**Task 3:** Pre-screen optimal MOF targets by identification of systems that produce an H_2 binding enthalpy > 20 kJ/mol	12%	Preliminary results indicate a number of potential targets
03/14	**Task 4:** Demonstration of a correlation between high-pressure measurements and theoretical and spectroscopic predictions	100%	Correlation demonstrated for several MOF-74 variants
06/14	**Task 4:** Demonstrate the ability to measure H_2 adsorption in a test material up to 10 cycles at 298 K	25%	On-track
09/14	**Task 4:** Demonstrate the ability to measure H_2 adsorption in a test material up to 10 cycles at t° relevant to onboard vehicle applications	10%	On-track
12/14	**Task 4:** Down select 1 or 2 samples for 100 cycles measurement	0%	Not started
03/15	**Task 4:** Demonstrate the ability to measure high-pressure H_2 adsorption in MOFs up to 100 cycles at temperatures relevant to use in onboard vehicle applications	0%	Not started

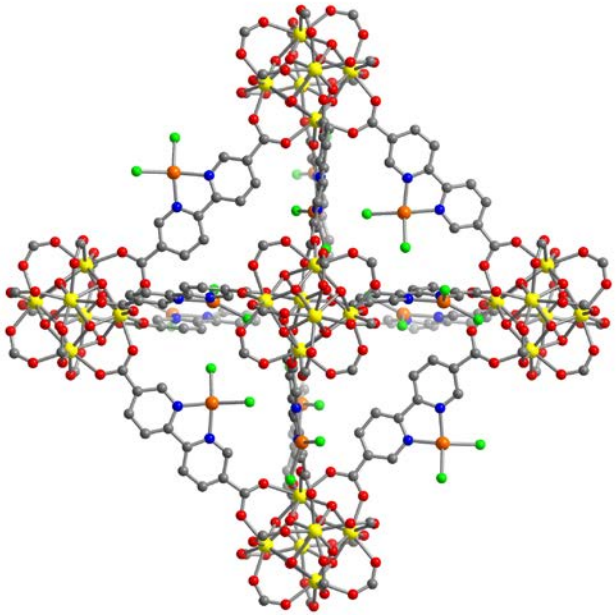
Accomplishments: Task 1
Synthesis of $Zr_6O_4(OH)_4(bpydc)_6$ (UiO-67-bipy)



MX_2, MeCN

1 day, 70 °C

MX_2 = $CoCl_2$, $MnCl_2$, $MnBr_2$, $FeCl_2$, $FeBr_2$, $CuCl_2$, $PdCl_2$



$Zr_6O_6(OH)_4(bpydc)_6$

SA_{BET} = 2645 m^2/g

$Zr_6O_6(OH)_4(bpydc)_6(MX_2)_6$

SA_{BET} = 1200-1800 m^2/g

- Single crystal X-ray diffraction unambiguously confirms metal insertion
- Gas adsorption experiments are ongoing

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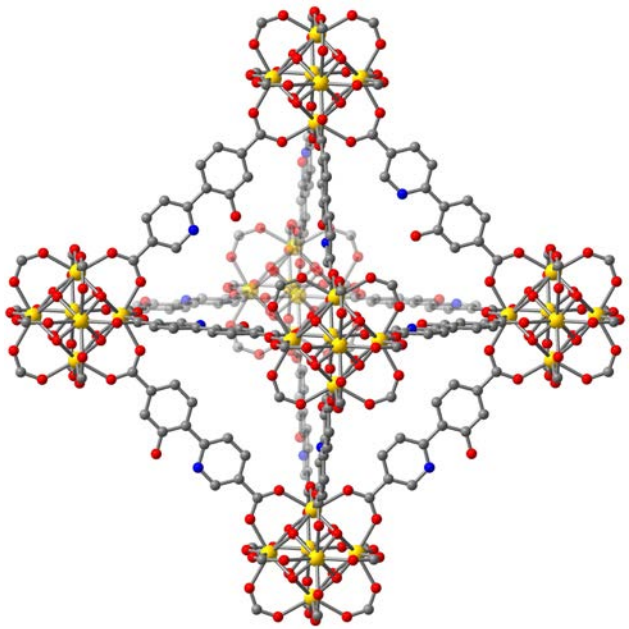
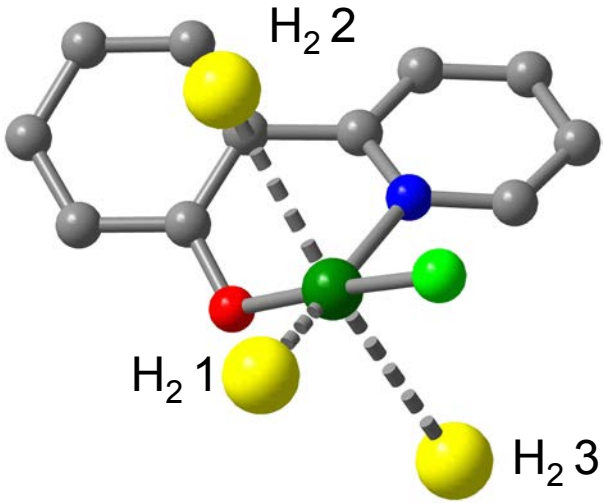
Accomplishments: Task 1
Synthesis of Charge Balancing UiO-67-bipy Analog



$Zr_6O_6(OH)_4(bpydc)_6$

SA_{BET} = 2715 m^2/g

$NiCl_2$ →



Predicted binding enthalpies:

H_2 1 = -16.8 kJ/mol

H_2 2 = -11.8 kJ/mol

H_2 3 = -9.6 kJ/mol

- Phenol group provides charge balance and access to multiple H_2/M^{2+}
- Robust framework is expected to accommodate high activation temperatures required for full desolvation of Ni^{2+} sites

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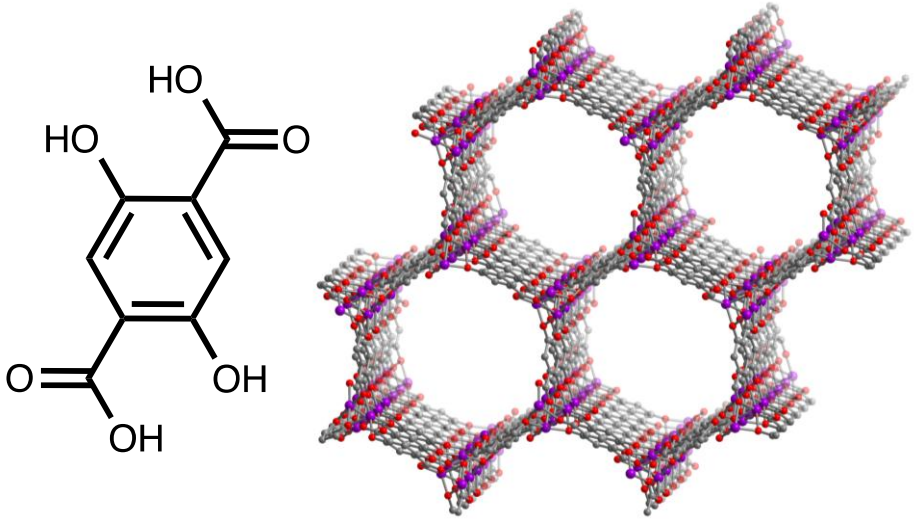
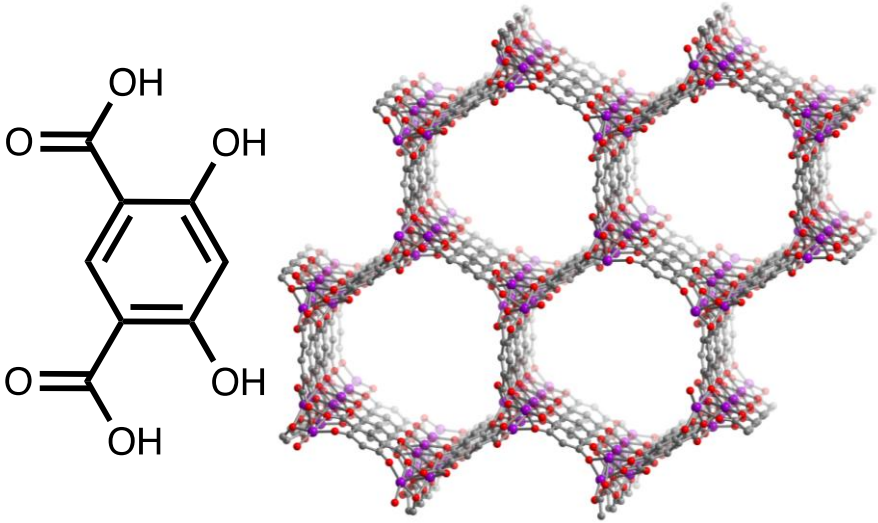
Accomplishments: Task 1
Synthesis and Characterization of M_2(*m*-dobdc)



M_2(dobdc)

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

SA_{BET} = 800-1750 m^2/g



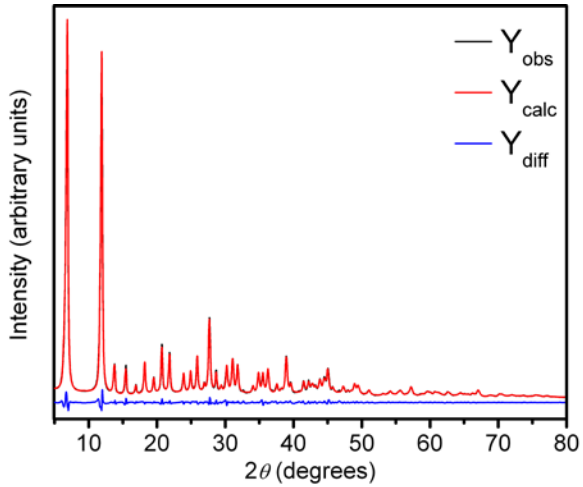
M_2(*m*-dobdc)

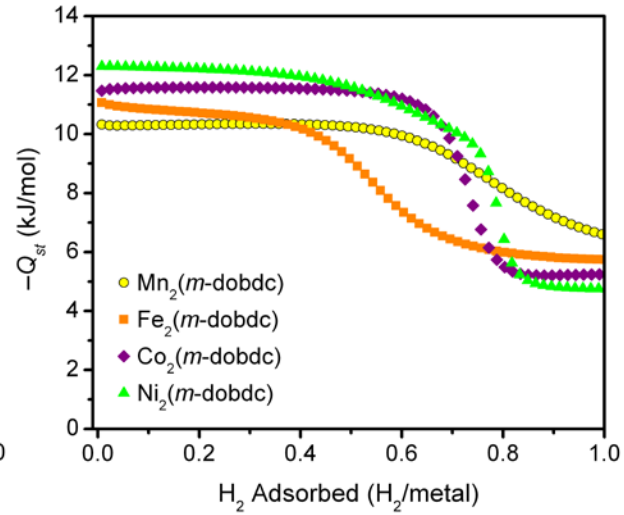
(M = Mn, Fe, Co, Ni)

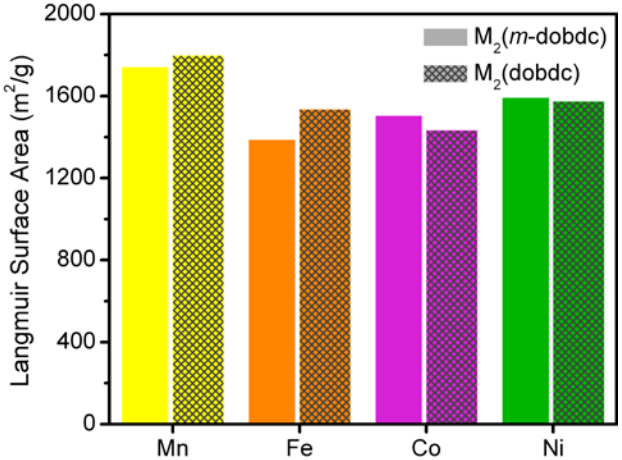
SA_{BET} = 1100-1600 m^2/g

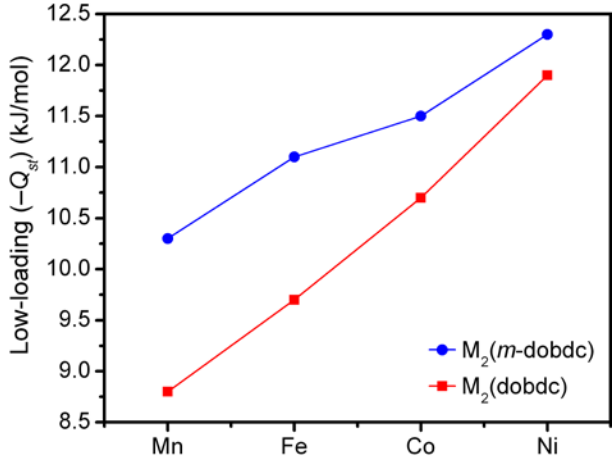
- Cheaper ligand via direct carboxylation of resorcinol
- Symmetry change of ligand is expected to impact H_2 adsorption properties

Accomplishments: Task 1
Synthesis and Characterization of M_2(*m*-dobdc)



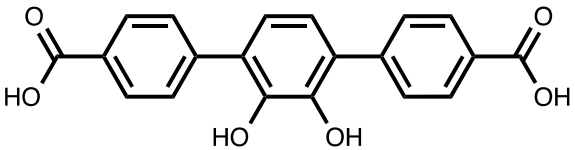


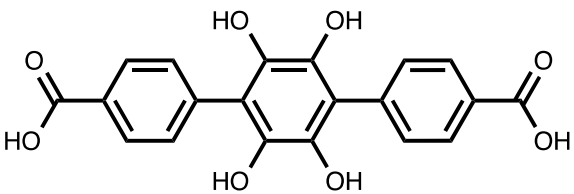


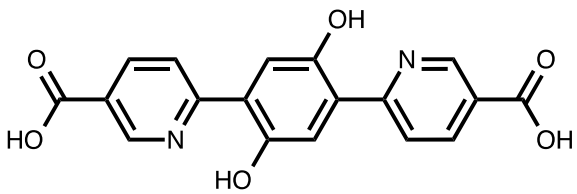


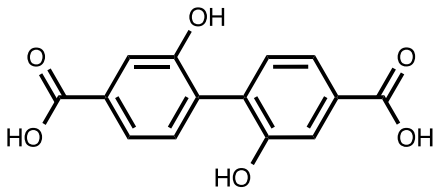
- High crystallinity enabled structure determination via powder x-ray diffraction
- M_2(*m*-dobdc) features comparable surface area to M_2(dobdc)
- M_2(*m*-dobdc) displays increased isosteric heat of H_2 adsorption

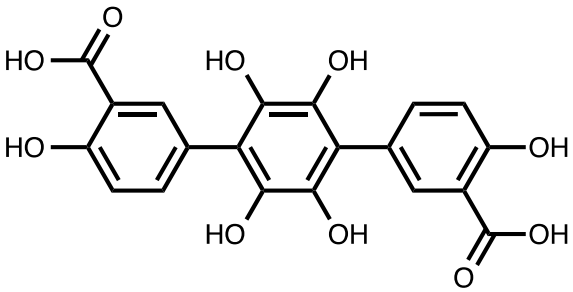
Accomplishments: Task 1
Synthesis of New Charge Balancing Ligands

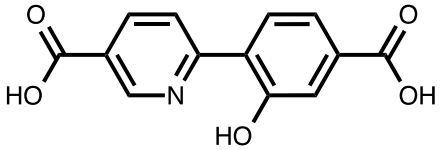


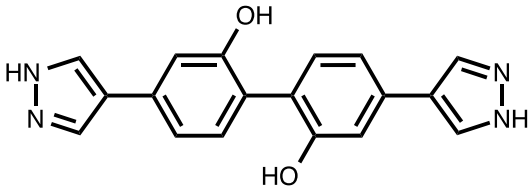


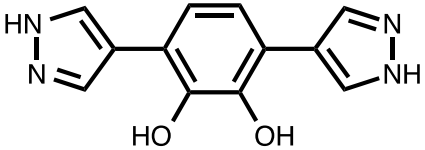


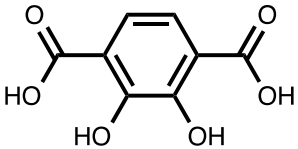






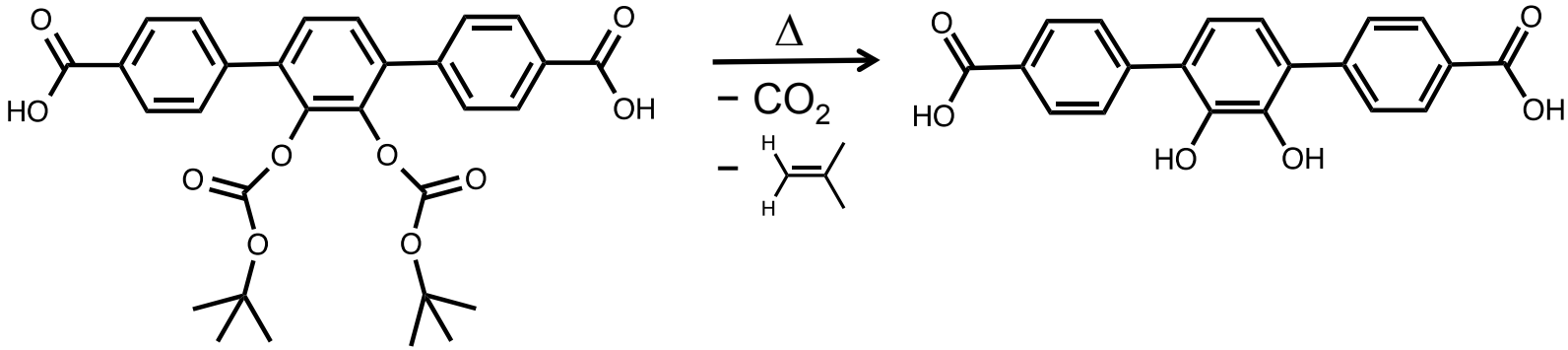




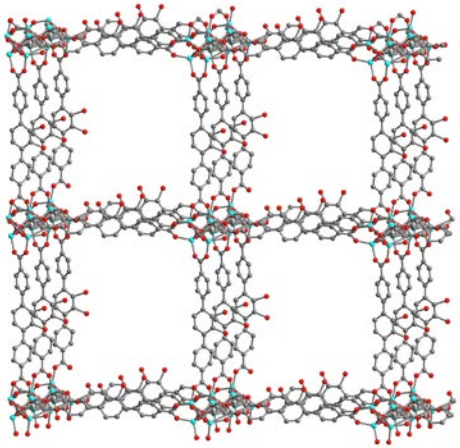


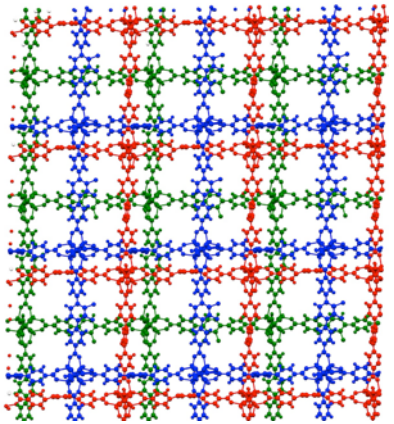
- These new ligands have all been synthesized and applied in MOF formation
- The resulting MOFs will be metallated to give M^{2+} cations with 4 open sites

Accomplishments: Task 1
Protecting Group Strategy



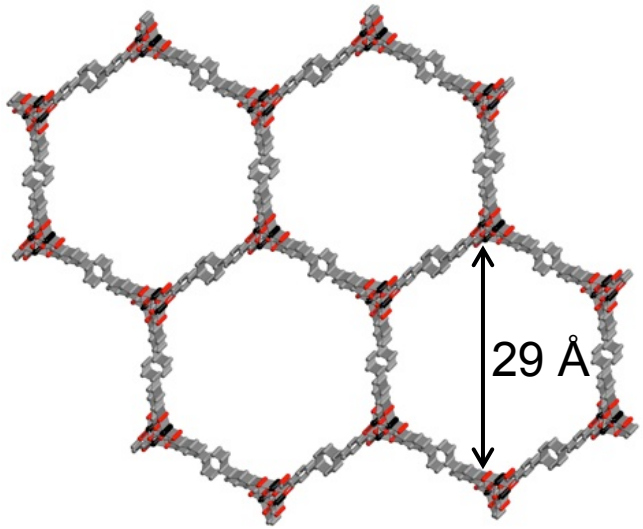
$Zn(NO_3)_2 \cdot 6H_2O$
DEF, 2.5 M NaOH
90 °C





- Protecting groups needed to block chelate sites during synthesis
- Bulky protecting groups may be used to control interpenetration

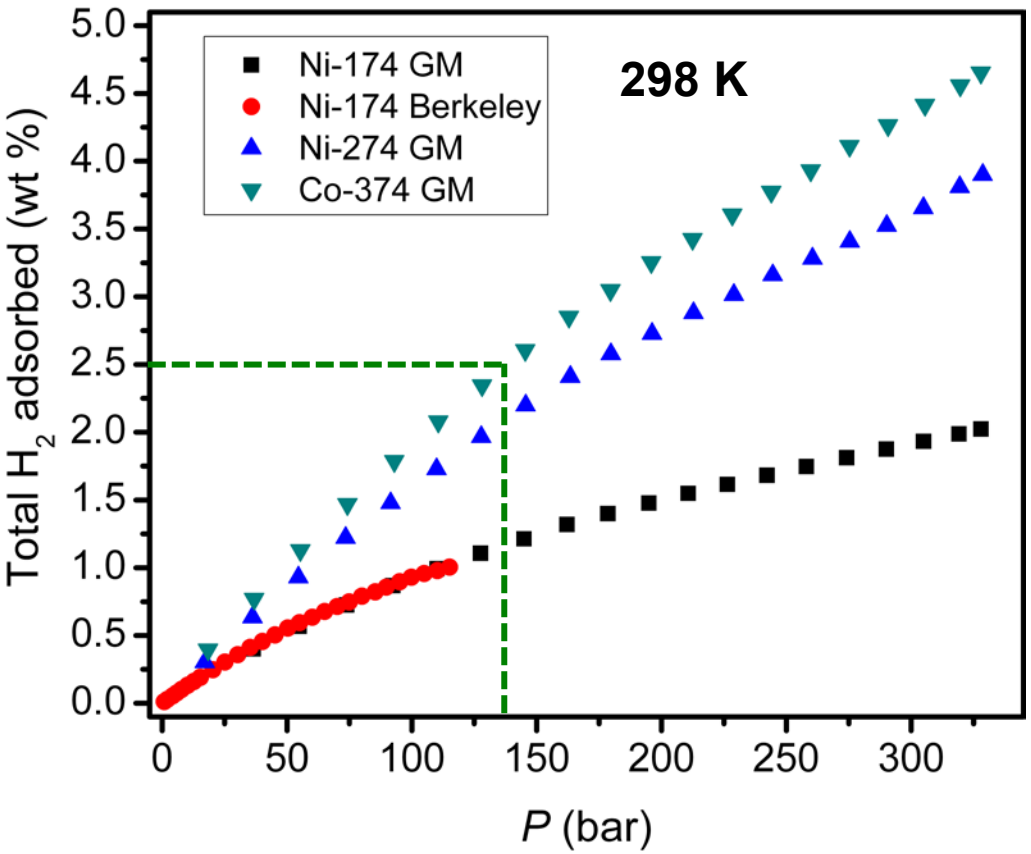
Accomplishments: Task 1
High-Pressure Adsorption in MOF-74 Analogues



M_2(dotpdc)

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

SA_{BET} = 2700-3600 m^2/g



- Co_2(dotpdc) reaches 2.5 wt % at 298 K and 140 bar
- Mg_2(dotpdc) is expected to reach 2.5 wt % by 100 bar

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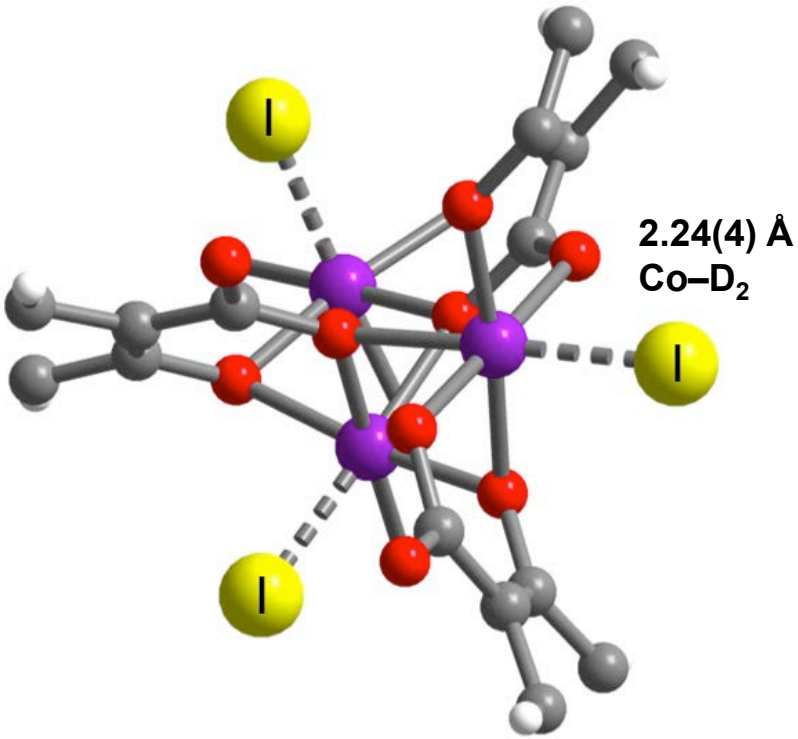
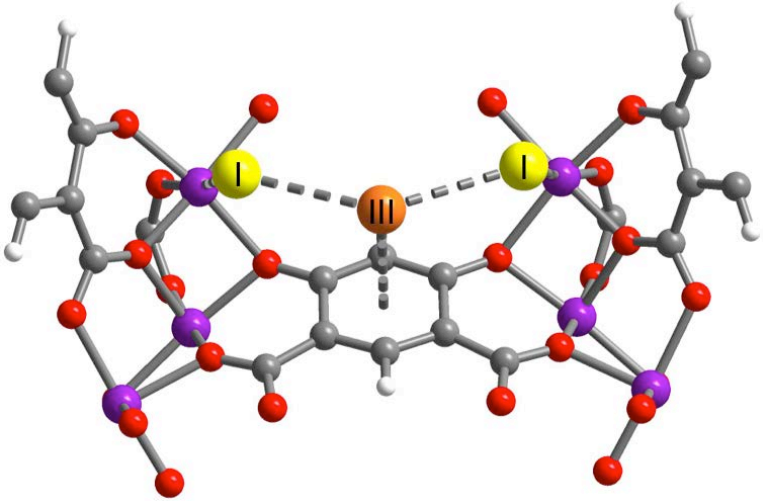
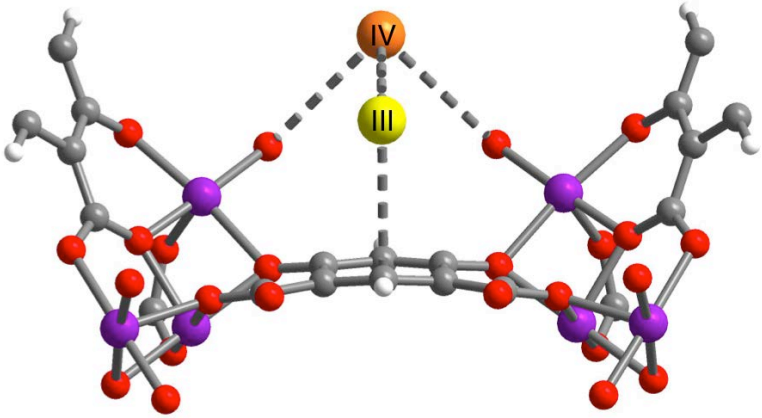
Accomplishments: Task 2
Neutron Powder Diffraction: D_2 in Co(*m*-dobdc)



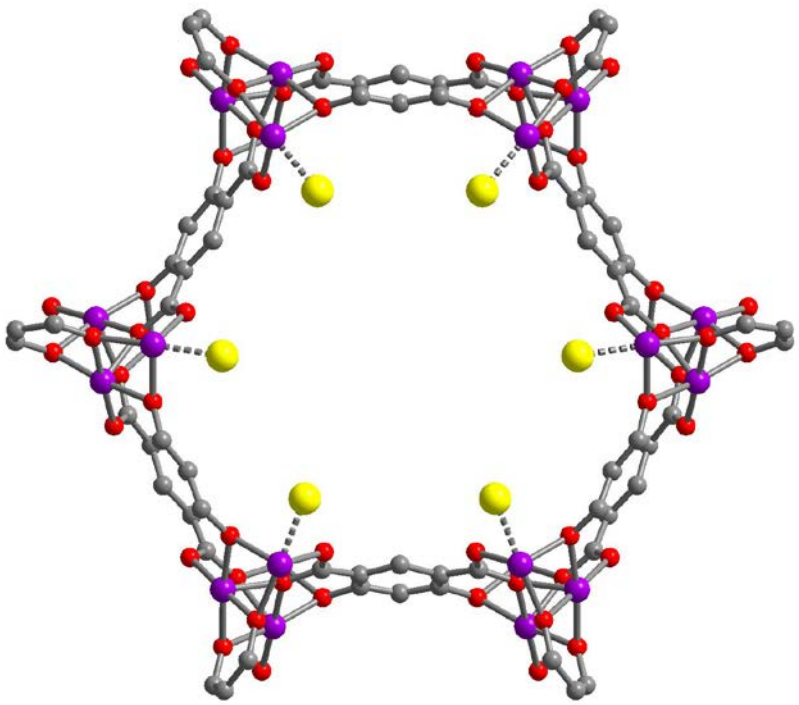


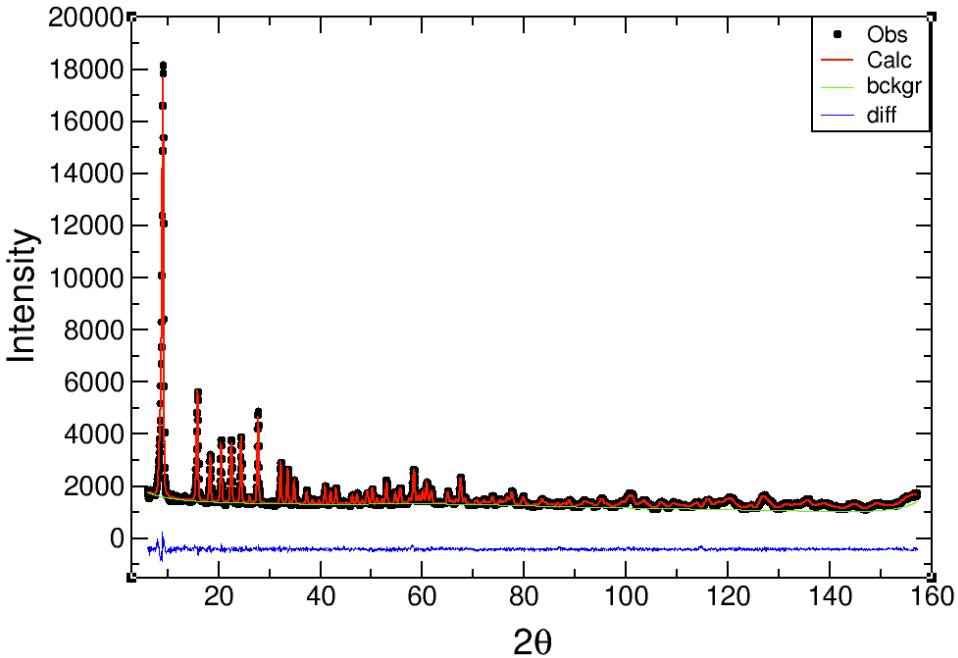


Co(*m*-dobdc) loaded with 0.75 D_2:Co
Initial adsorption at metal sites with Co···D_2 distance 2.24(4) Å

Accomplishments: Task 2
Neutron Powder Diffraction: D_2 vs H_2

First structure for H_2 adsorbed in a MOF
Typically D_2 is used due to much lower inelastic scattering cross section





Low loading (0.5 per metal) binding sites are the same with slight distance difference

Co—D_2 = 2.23(5) Å

Co—H_2 = 2.27(3) Å

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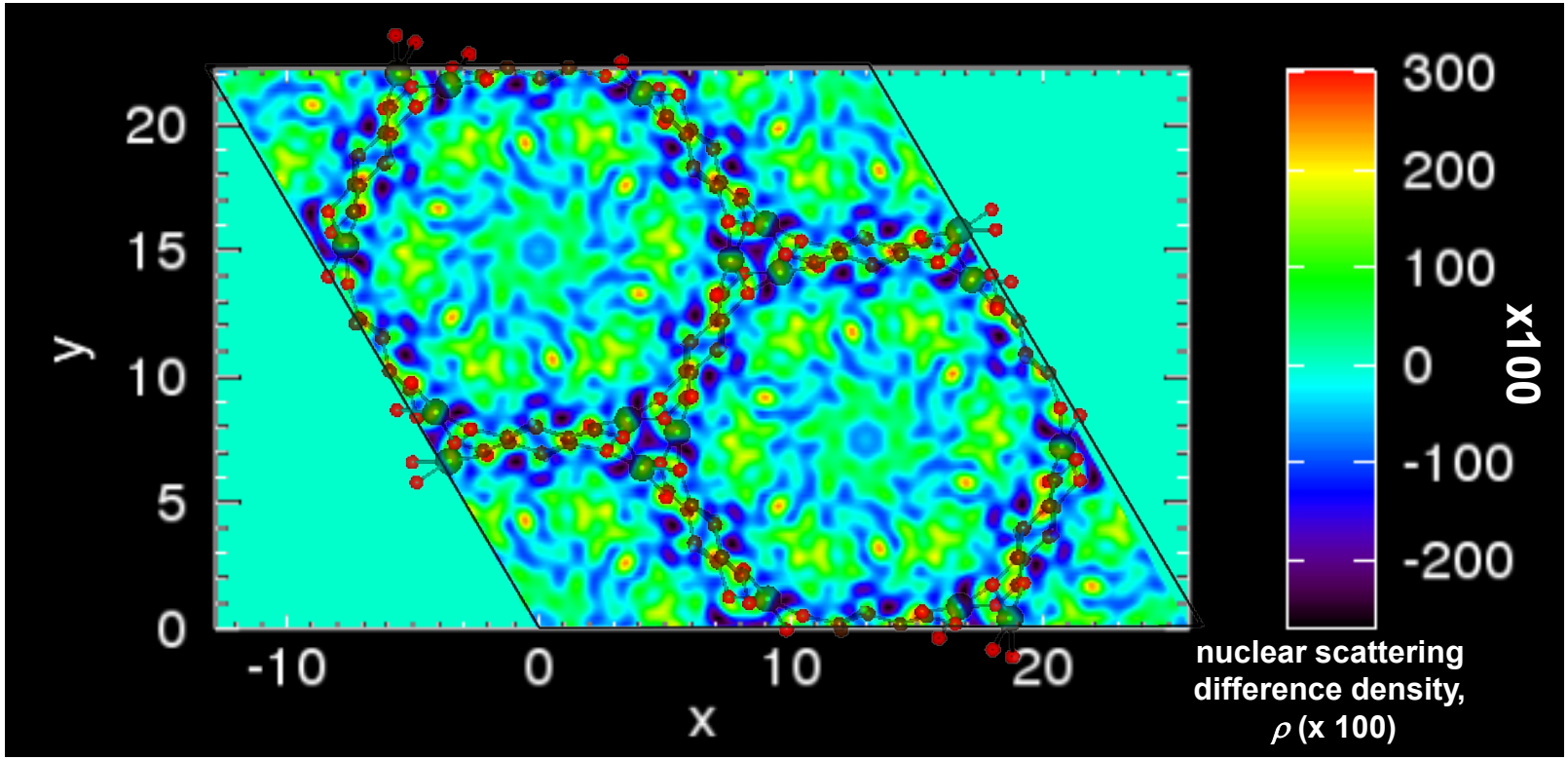
Accomplishments: Task 2

Neutron Powder Diffraction: High Pressure D_2 Adsorption



- Difference Fourier map obtained from pattern of 90 bar D_2 in Zn(dobdc) at 77 K
- Attempting to image hydrogen density in pore at relevant pressures and temps
- Maximum-Entropy data interpretation and measurements are ongoing

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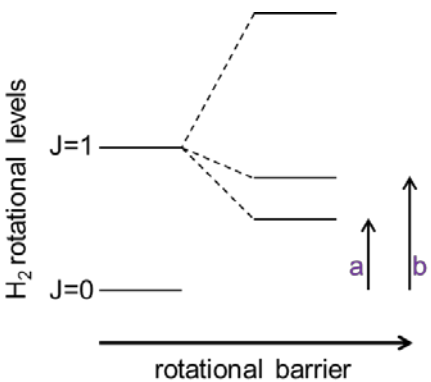
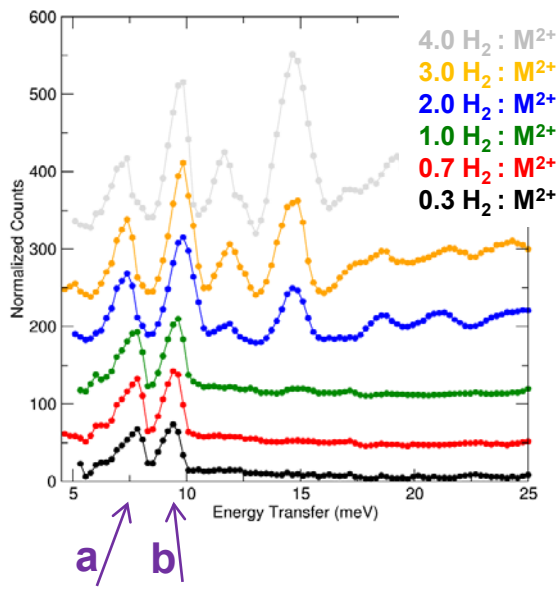
Accomplishments: Task 2
Inelastic Neutron Scattering Data for M_2(*m*-dobdc)

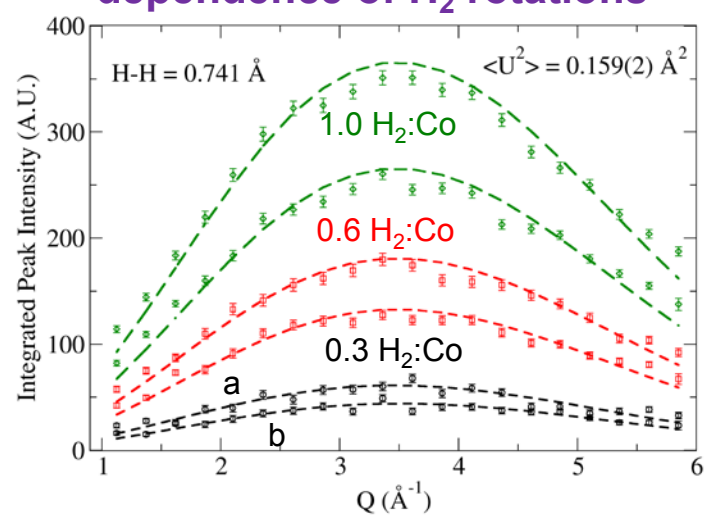


Data from BT-4 and DCS, NIST Measured at 10 K

Co(*m*-dobdc)



Measured vs. Theoretical momentum transfer dependence of H_2 rotations



$$I(Q) \propto e^{(-Q^2<u^2>/3)} j_1(d_{HH}Q/2)^2$$

- Rotational barrier at first adsorption site indicates that the *m*-dobdc materials have similar characteristics compared to dobdc materials
- Local adsorption potential is weaker with further filling
- Correlates with diffraction and isotherm data
- Q-dependence indicates an almost ideal H-H molecule adsorbed at the metal

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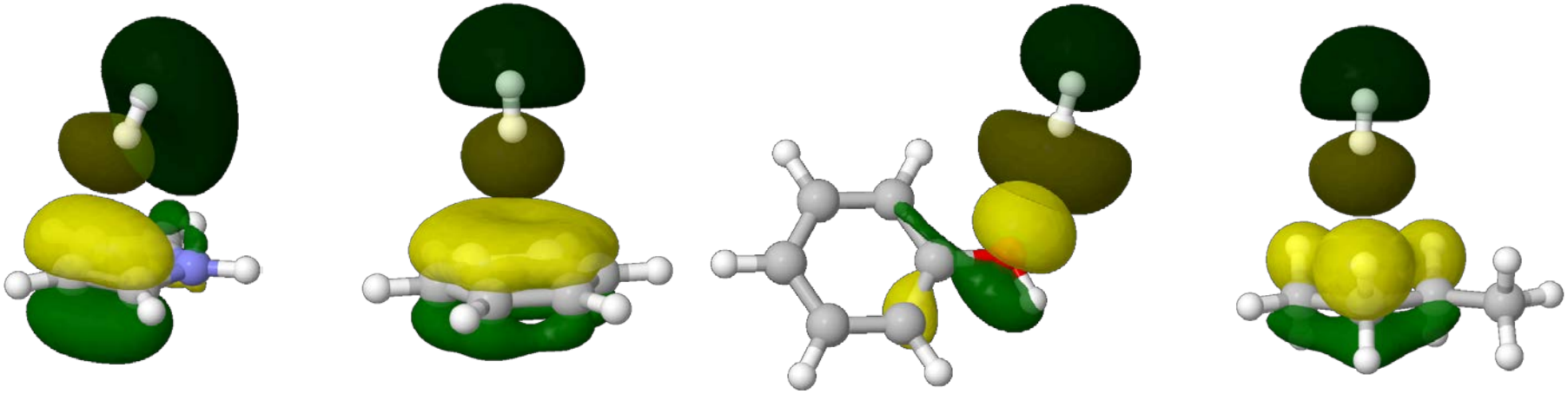
Accomplishments: Task 3
Calculation of Ligand-H_2 Interactions



Pyrrole
-2.07 kJ/mol

Benzene
-1.42 kJ/mol

Phenol
-0.93 kJ/mol

Butene
-1.35 kJ/mol

- Nonnegligible charge transfer between bare ligand/H_2
- To maximize H_2 adsorption enthalpy both metal-H_2 and ligand-H_2 interactions must be considered

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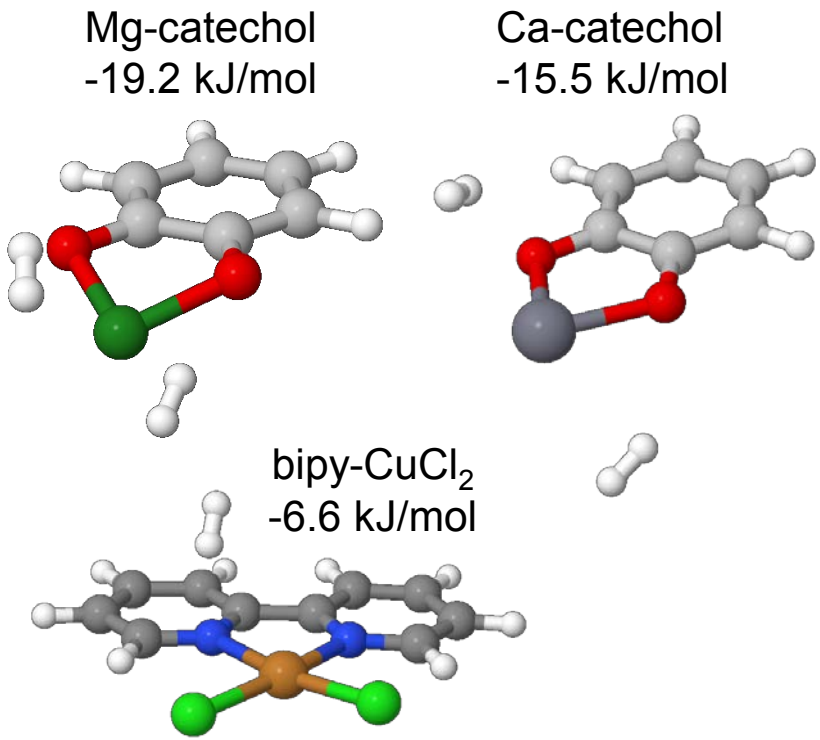
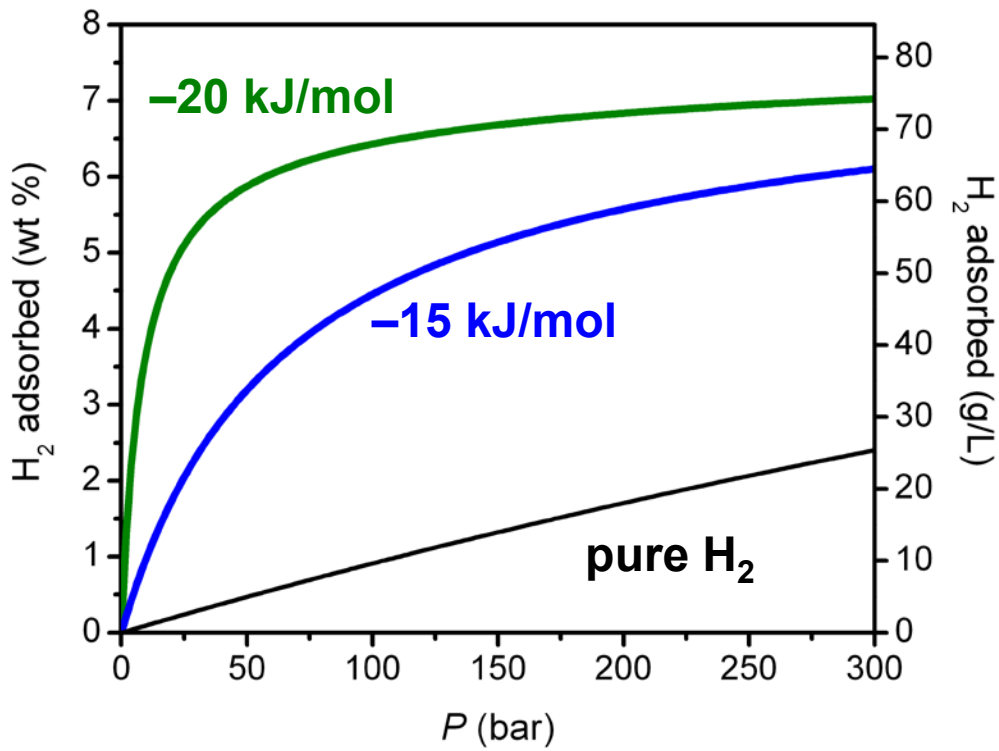
Accomplishments: Task 3
Calculation of H_2 Binding Enthalpies



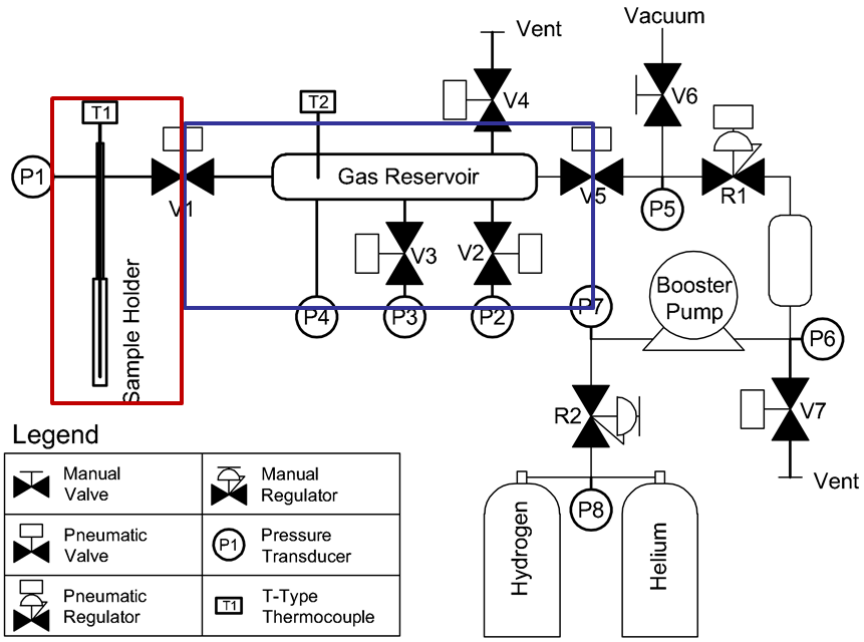


- Calculated average H_2 binding enthalpies for free Mg- and Ca-catechols indicate 15-20 kJ/mol are attainable
- Although metals coordinated to bipyridine have two open coordination sites the predicted H_2 binding enthalpy is low

Accomplishments: Task 4
High Pressure H_2 Adsorption System

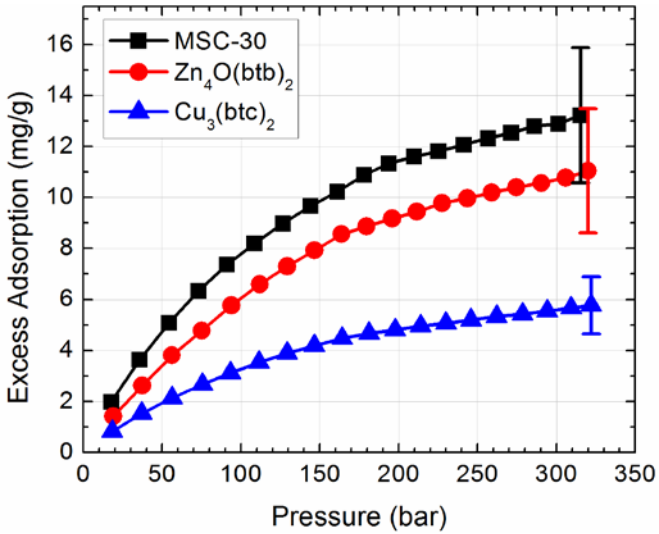
System Specifications

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



Challenges of 350 bar H_2 measurements

- Careful system calibration
- 0.05 cm^3 reference volume error results in 0.5 mmol deviation at 350 bar
- 0.5 g of MSC-30 adsorbs ~3 mmol H_2 at 350 bar and 298 K



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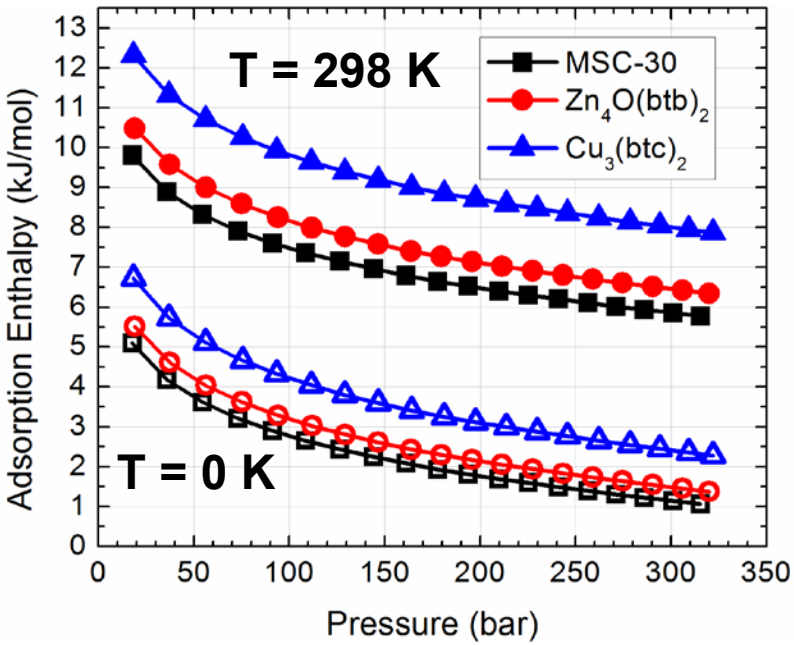
Accomplishments: Task 4
Evaluation of Materials

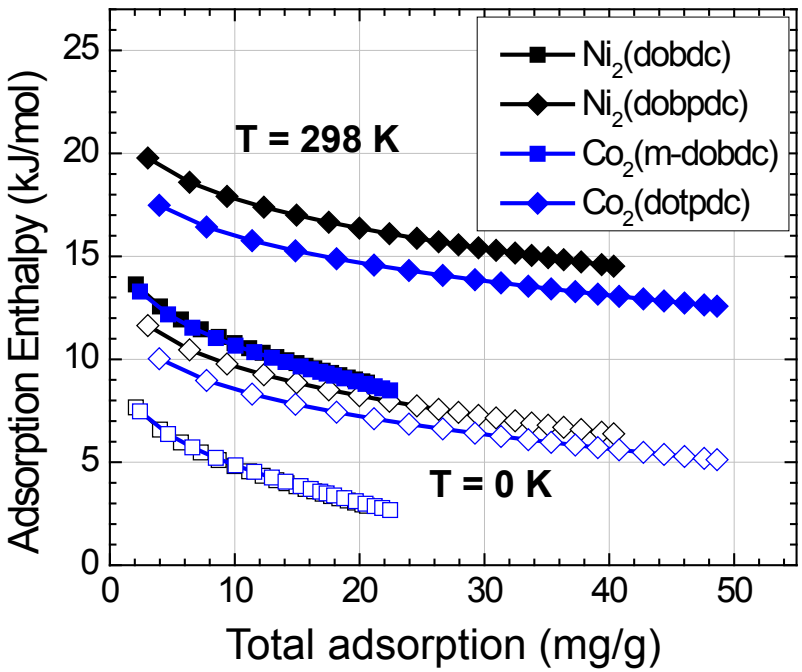
Adsorption Enthalpy from One Isotherm

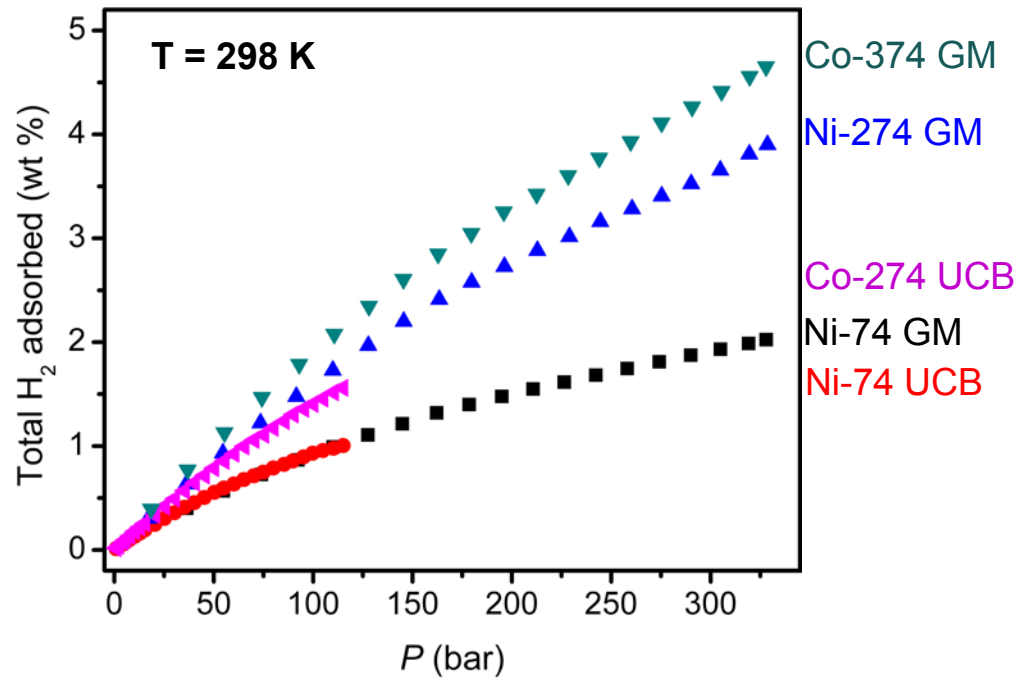
- Apply van't Hoff formula directly to the Dubinin-Astakhov model
- Empirical temperature independent constants are used
- Results for benchmark materials are consistent with expectations



Am. J. Analytical Chem. ***2013****, 4,* 8-16.

Accomplishments: Task 4
Evaluation of New Materials





- Expanded MOF-74 analogues feature increased gravimetric H_2 uptake
- M_2(dotpdc) frameworks reach 2.5 wt. % total at 298 K, 140 bar

Accomplishments and Progress: Responses to Previous Year Reviewers' Comments

- As specified on Slide 3, our focus is on the creation of materials that can help meet the 2017 system capacity targets of 5.5% H_2 by mass, volumetric capacity of 40 g/L
- We have in fact collected H_2 uptake at both low and high pressures and various temperatures for dozens of new MOFs, but these results were summarized rather showing the isotherms owing to presentation time restrictions. A few selected data sets are now depicted Technical Back-Up Slides 31-34.
- Our overall strategy, as summarized on Slide 5, is to create materials with a high-density of open M^{2+} or M^{3+} cation sites, each capable of binding 4 or 5 H_2 molecules. This is the only viable route we see to meeting the volumetric capacity target of 40 g/L in a MOF.
- Our roadmap to accomplishing this involves the synthesis of thermally robust MOFs containing anionic chelating sites that can then be metallated and fully activated.
- We agree that the very high-pressure measurement system at GM is unnecessary if we achieve our goals. However, the instrument has already been installed and it enables validation and extension of the high-pressure data collected at Berkeley.

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:

- Variable-temperature infrared spectroscopy with *in situ* H_2 dosing
  - Silvia Bordiga (University of Turin), Stephen FitzGerald (Oberlin College)
- Synthesis and metallation of porphyrin-containing MOFs
  - T. David Harris (Northwestern University)

Remaining Challenges and Barriers

- Charge balancing ligands have been realized, however, optimal metallation and activation procedures need to be discovered.
- Correlation between OSAD program selected materials and experimentally promising frameworks needs to be realized.
- Gravimetric storage capacity targets have been achieved at pressures higher than 100 bar and/or temperatures below 298 K. New Mg^{2+} based materials should address these issues.
- While theoretical predictions have suggested optimal metallation targets, experimental realization must be achieved to confirm theoretical results.

Proposed Future Work

Task 1: Synthesis of Metal-Organic Frameworks

- Determine optimal metal-insertion and activation conditions for pyridine/phenol ligand
- Scale up synthesis of catechol containing MOFs and insert metal cations
- Complete synthesis of expanded MOF-74 analogues with Mg^{2+}
- Continue synthesis of catechol based ligands for metal insertion.

Task 2: Characterization of Framework-H_2 Interactions

- Solve structure of $Zr_6O_4(OH)_4(bpydc)_6(PdCl_2)_6$
- Complete neutron powder diffraction experiments on this material as 2 H_2 molecules per Pd^{2+} should be possible
- Continue inelastic neutron scattering experiments
- Perform quasielastic neutron diffraction experiments to study diffusion and entropy effects on H_2 adsorption

Proposed Future Work

Task 3: First-Principles Calculations of Hydrogen Binding Enthalpies

- Explore H_2-Metal interactions in real systems that have been realized experimentally
- Determine optimal metallation conditions for charge balancing ligands, investigating solvation effects solvent binding enthalpies.
- Pre-screen optimal targets to identify potential H_2 binding sites greater than 20 kJ/mol.

Task 4: High-Pressure H_2 Adsorption Measurements

- Measure high-pressure H_2 adsorption on samples up to 10 cycles.
- Down select 1-2 materials for 100 adsorption/desorption cycles.
- Test high performing MOFs for 100 cycles up to 350 bar

Summary

- Expanded MOF-74 analogues have achieved 2.5 wt.% total adsorption at 140 bar
- A new mixed pyridine/phenol ligand has been incorporated into a zirconium based framework and has been shown to bind divalent metals.
- Four MOF-74 isomers have been synthesized and characterized and show increased H_2 binding enthalpies.
- Neutron diffraction experiments have been performed using H_2.
- Theoretical calculations have been used to predict metallation targets.
- High-pressure isotherms have been used to calculate H_2 binding enthalpies up to 320 bar.

Capacity	2012	2013	2014	2017*	Ultimate*
Gravimetric	0.016 kg H_2/kg adsorbent	0.016 kg H_2/kg adsorbent	0.022 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	0.011 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

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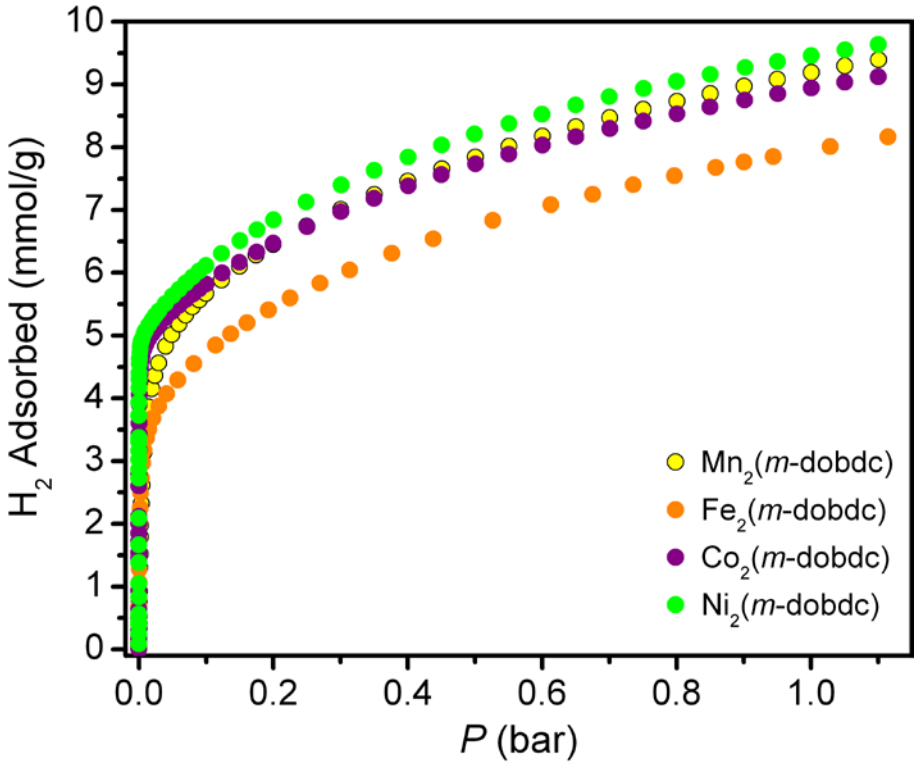
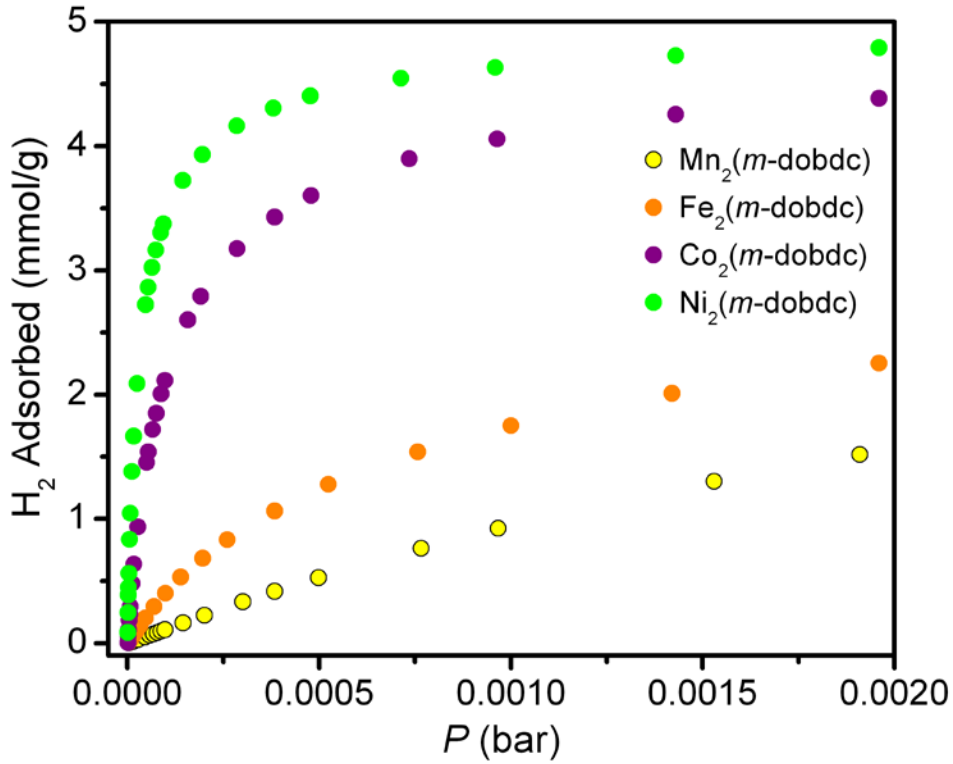
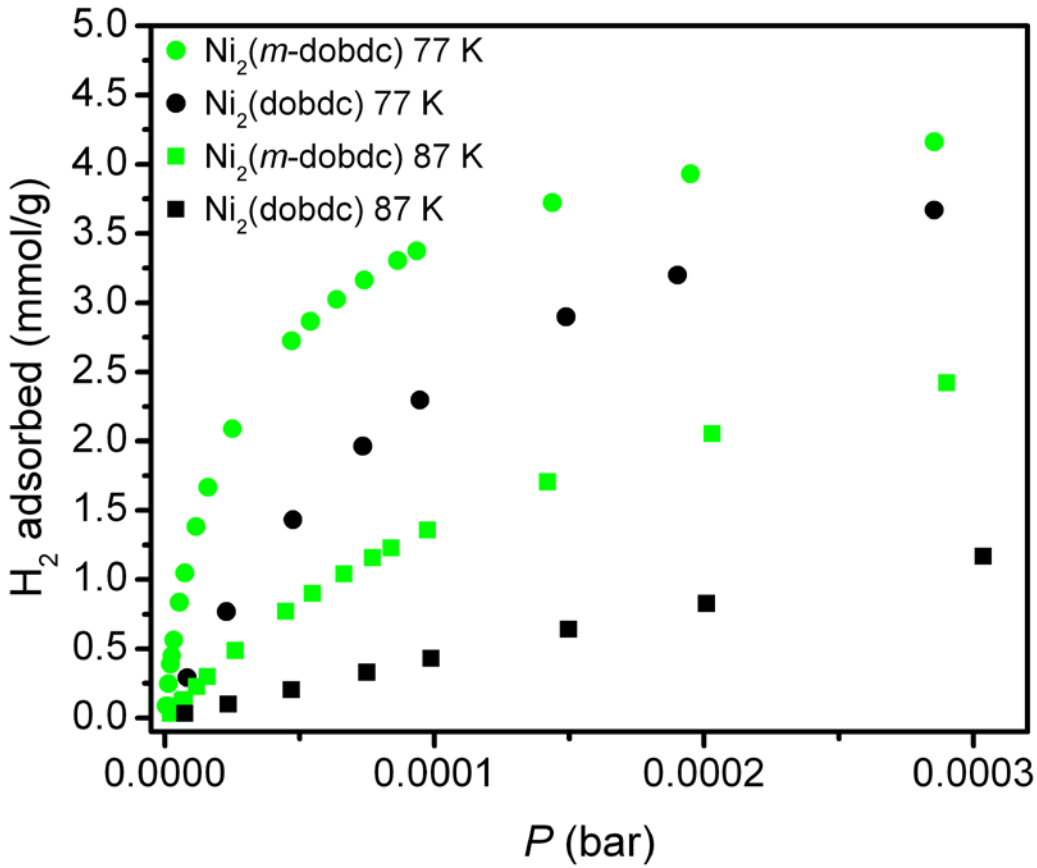
Adsorption Isotherms
M_2(*m*-dobdc)





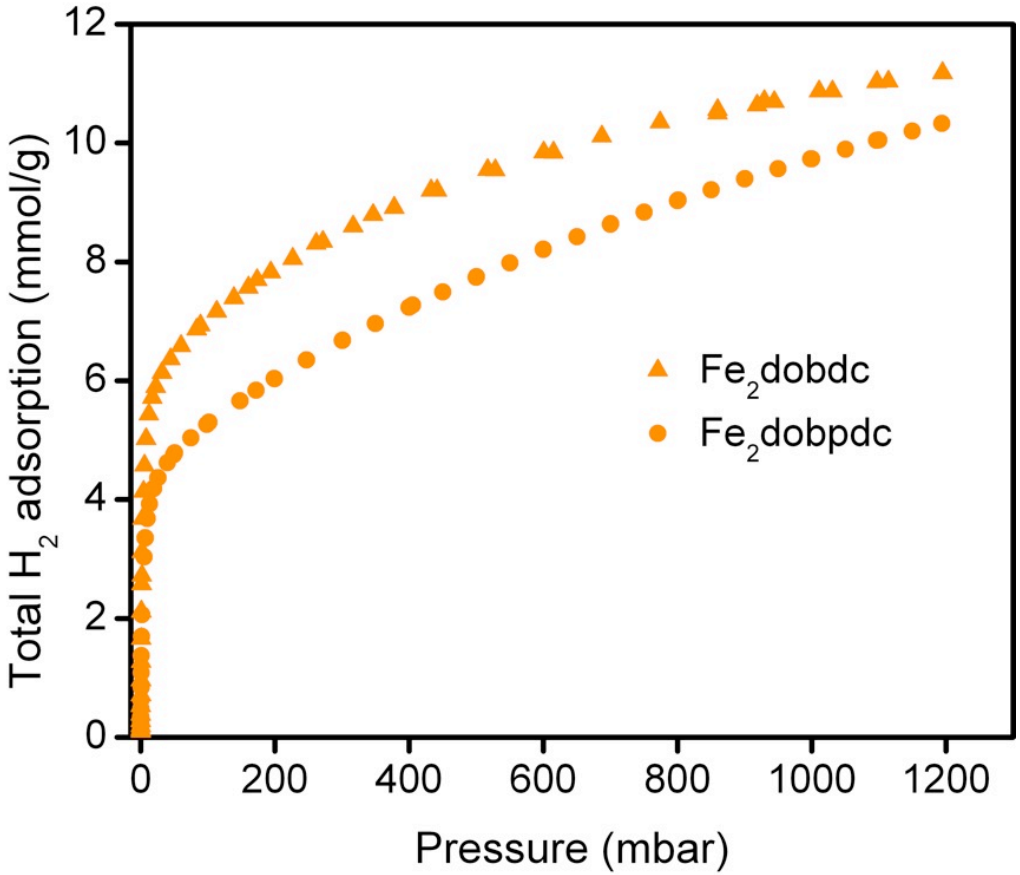
- Although $-Q_{st}$ follows Ni > Co > Fe > Mn, saturation capacity at 77 K and 1.2 bar doesn't follow the trend as surface area factors into total uptake

Adsorption Isotherms



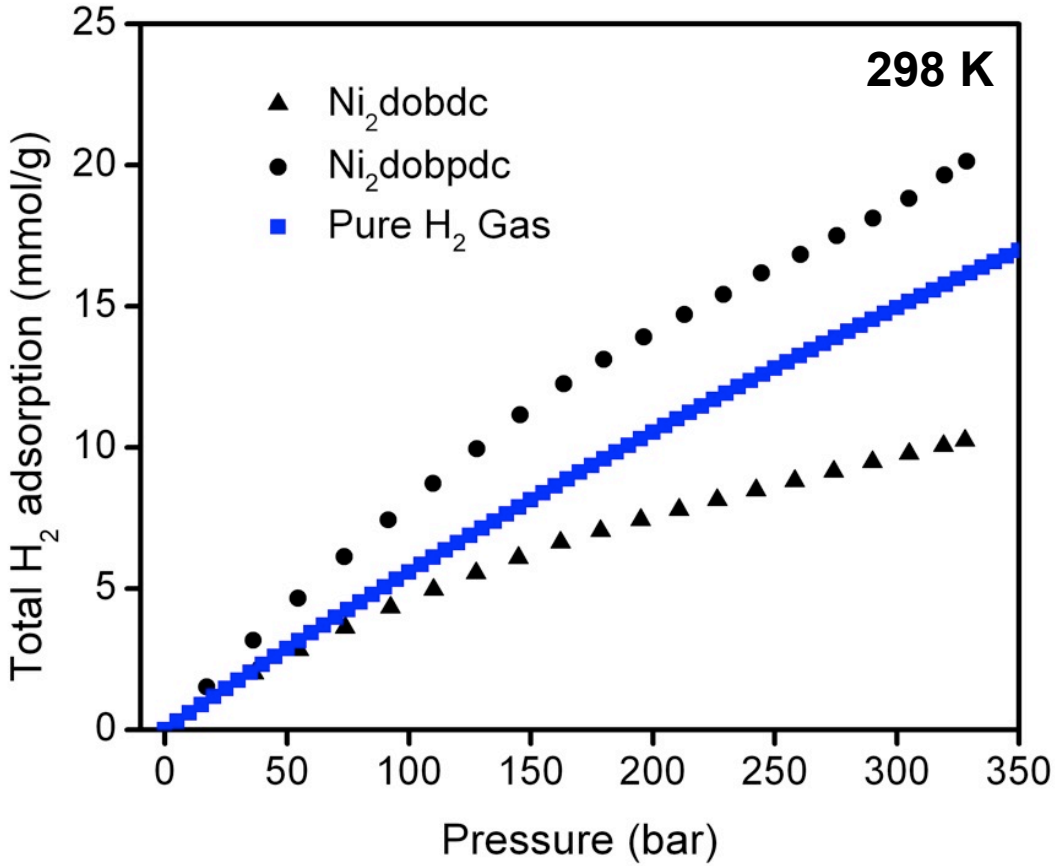
- Adsorption isotherms for Ni_2(*m*-dobdc) are steeper than the *para* isomer, indicating a stronger M-H_2 interaction.

Adsorption Isotherms
M_2(dobdc) vs. M_2(dobpdc)



- Given the larger density of coordinatively-unsaturated metal sites, M_2(dobdc) displays higher H_2 capacity at 1.2 bar and 77 K.

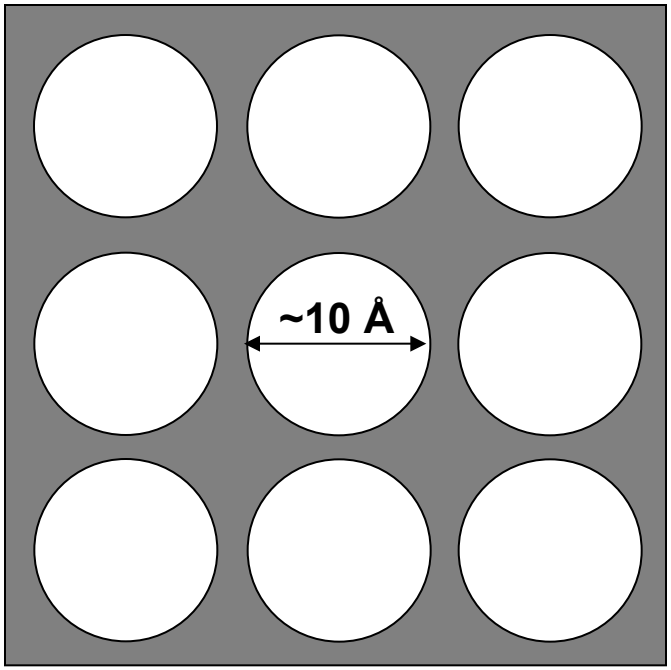
Adsorption Isotherms
M_2(dobdc) vs. M_2(dobpdc)



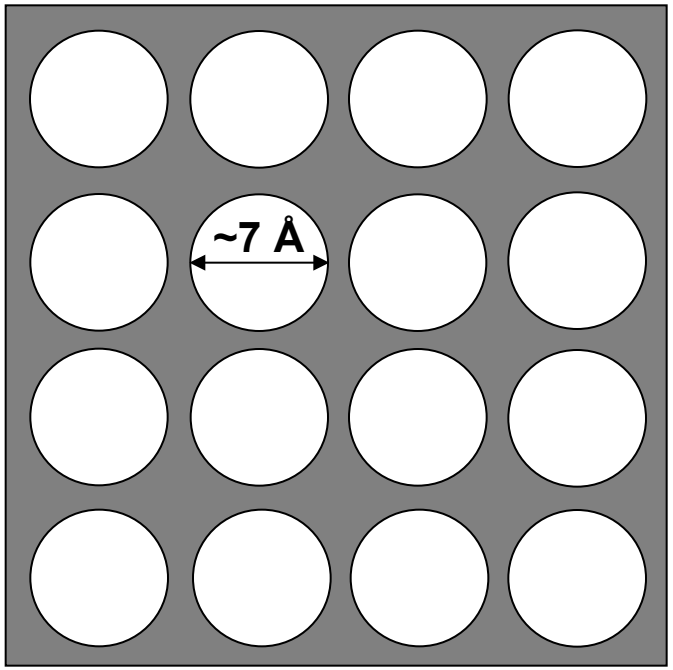
- At high pressure, M_2(dobpdc) significantly outperforms M_2(dobdc) and offers a significant improvement over compressed H_2.

Optimum Pore Sizes for Hydrogen Storage

77 K



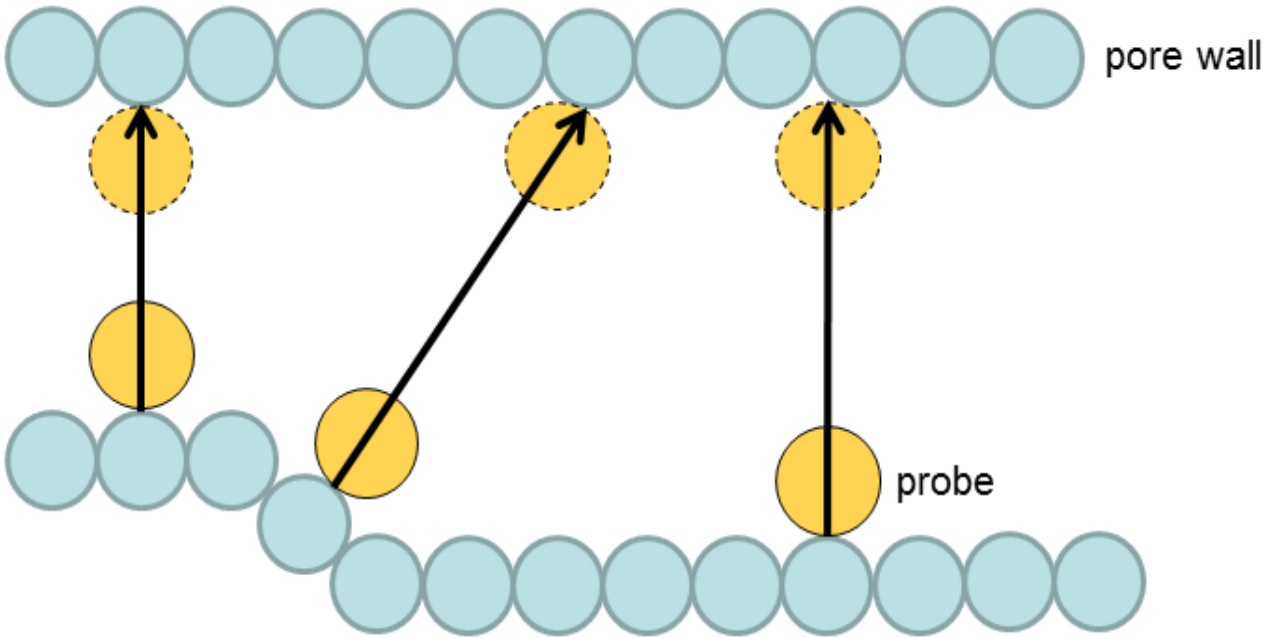
298 K



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

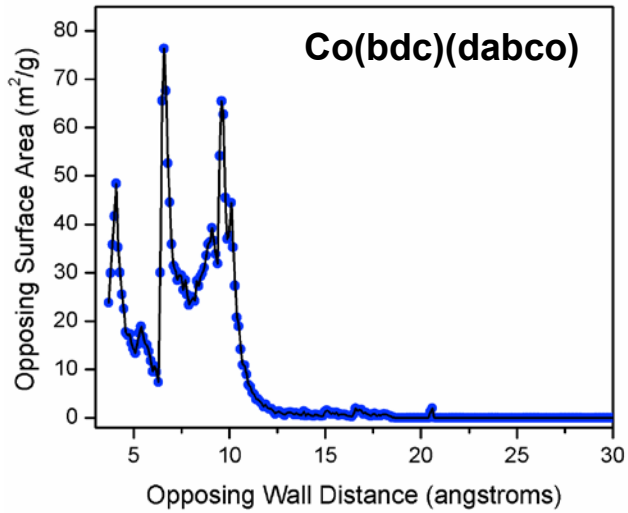
Rzepka, Lamp, de la Casa-Lillo J. *Phys. Chem. B* **1998**, *102*, 10894

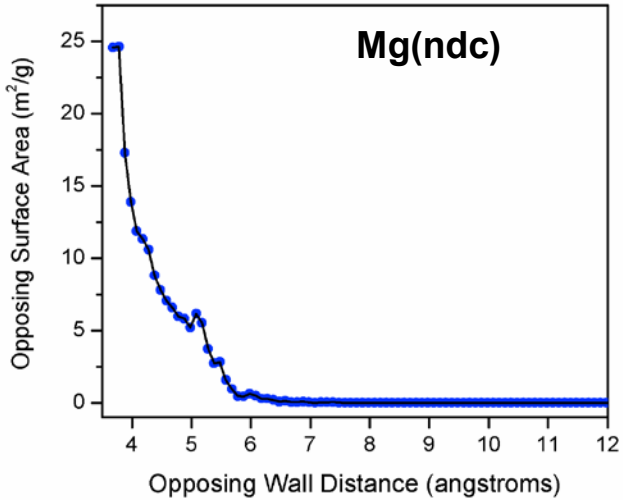
Geometric Calculation of Opposing Wall Distances

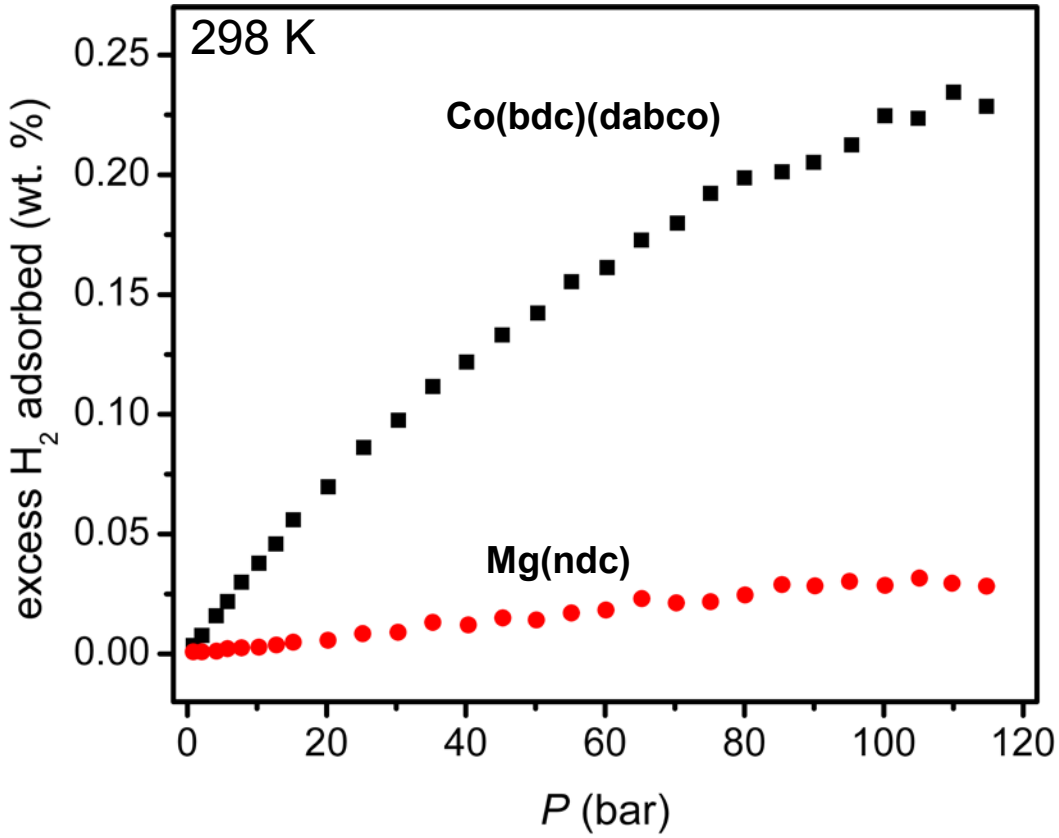


- Probe is inserted on the pore surface, and moved away in a direction normal to the surface until it collides with the opposing wall
- This is repeated until the entire pore surface has been traversed by the algorithm to create a distribution of opposing wall distances

Opposing Surface Area Distribution (OSAD)







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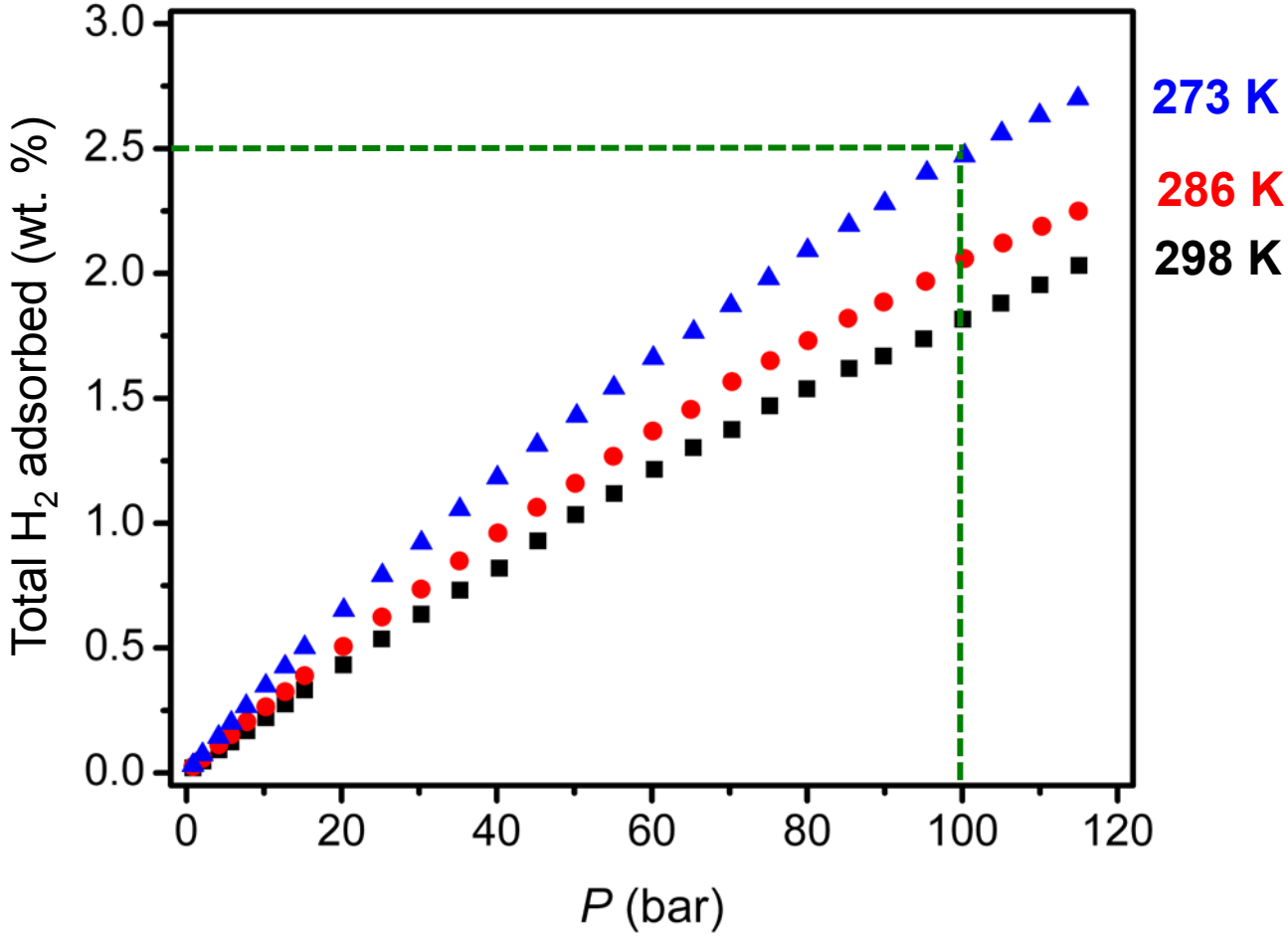
High-Pressure H_2 Adsorption



- Mg_2(dobpdc) achieves 2.5 wt. % target at 273 K, 100 bar.

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